

Scaling properties of diffusion-limited reactions

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A simple scaling argument for diffusion-limited reactions for both $A + A \rightarrow 0$ and $A + B \rightarrow 0$ is developed. Temporally asymptotic behavior of species densities in the absence of sources and reaction orders in the steady state in the presence of sources are discussed. We specifically address the effect of the spatial distributions of reactants on the reaction rates. For the $A + A \rightarrow 0$ reaction we recover existing results found by other methods. For $A + B \rightarrow 0$ in the absence of sources we find that the asymptotic behavior depends not only on the spectral dimension (as commonly believed) but also on the fractal dimension. In the presence of sources we agree with previous results when the steady-state density is not too low, but argue that a modification of these results may occur at very low densities.

I. INTRODUCTION

Diffusion-controlled annihilation reactions of the form $A + A \rightarrow 0$ and $A + B \rightarrow 0$ are known to obey kinetic laws that differ from the "classical" mean-field forms in low-dimensional systems. These deviations arise from the fact that the spatial distributions of reactants differ from the thoroughly mixed ones that are implicit in the usual mass-action rate laws. In the $A + A \rightarrow 0$ reaction, the differences between classical and "anomalous" behavior reflect the deviation of the distribution of nearest-neighbor distances from the Hertz form that underlies the classical rate law.¹ In the $A + B \rightarrow 0$ reaction, the anomalous behavior comes about because of the formation of segregated A -rich and B -rich aggregates that are not mixed by the diffusion mechanism in low dimensions. The precise forms of the deviations from classical behavior and the critical dimensions for these deviations depend on the reaction and on the presence and nature of reactant sources.²⁻⁸ Most theoretical analyses of the problem begin with Euclidean spaces of dimension d , and the extension to fractal spaces is carried out by replacing d with the spectral dimension d_s . For $A + A \rightarrow 0$, whether or not there are sources present, the critical dimension is 2 .⁸⁻¹¹ For $A + B \rightarrow 0$, existing results in Euclidean spaces in the absence of sources lead to the critical dimension, $d = 4$.^{2-5,12} The simple replacement of d with the spectral dimension leads to the conclusion that anomalous behavior occurs when $d_s < 4$. In the presence of sources, the critical dimension is $d = 2$,^{6,7,12} and the usual generalization to fractal structures¹³ leads to the conclusion that anomalous behavior should be observed when $d_s < 2$.

Herein, we present a simple scaling argument to deal with the reactions $A + A \rightarrow 0$ and $A + B \rightarrow 0$ in the presence and absence of sources. For the $A + A \rightarrow 0$ reaction, we recover existing results in a straightforward way.

In particular, we agree with the extension of Euclidean results to fractal structures via the simple expedient of replacing d with d_s . For the $A + B \rightarrow 0$ case, however, we do not agree with this recipe. Rather, we find that in the absence of sources the decay of the density in the anomalous regime and the critical dimension for anomalous behavior depend not only on the spectral dimension d_s but also on the fractal dimension d_f . In the presence of sources, we recover the usual results when the steady-state density is not too small (i.e., when the sources are not too weak); but we argue that modifications to these results may be necessary for very low steady-state densities.

II. NO SOURCES: ASYMPTOTIC BEHAVIOR

In this section we use scaling arguments to deduce the global rate laws for the diffusion-limited reactions $A + A \rightarrow 0$ and $A + B \rightarrow 0$ in the absence of sources. The only source of reactants is their initial distribution. For $A + B \rightarrow 0$, we consider only the case of equal initial numbers of the two species, an equality that of course continues for all time.

A. Single species: $A + A \rightarrow 0$

To find the asymptotic time-dependent behavior of the density of the species A in the diffusion-limited reaction $A + A \rightarrow 0$, we write the density as

$$\rho \sim t^{-\alpha}, \quad (1)$$

where α is an exponent to be determined. The rate of the reaction R_{AA} is related to the lifetime τ of each particle; in a diffusion-limited reaction the lifetime, in turn, is the time needed for a particle to diffuse to its nearest neighbor. The rate of the reaction also depends on the number N of nearest-neighbor pairs. These dependences are indi-

cated in the relation

$$R_{AA} \sim -\frac{d\rho}{dt} \sim t^{-\alpha-1} \sim N \frac{1}{\tau}, \quad (2)$$

where we have used (1). The number N of nearest-neighbor pairs is proportional to the number of A 's in the system. Since we are only interested in the order of the different terms for scaling purposes, we can simply write

$$N \sim \rho. \quad (3)$$

Regardless of dimension, the distinct number of sites visited, S , before a particle reaches its nearest neighbor (i.e., before it reacts) is of order

$$S \sim \rho^{-1}. \quad (4)$$

On the other hand, it is well known that the distinct number of sites visited by a walker increases with the elapsed time t_{el} as¹⁴

$$S \sim t_{\text{el}}^f, \quad (5)$$

where

$$f = \begin{cases} \frac{d_s}{2} & \text{for } d_s < 2, \\ 1 & \text{for } d_s > 2, \end{cases} \quad (6)$$

with d_s defined as the spectral dimension. Equation (6) reflects the fact that the walk executed by a particle is compact when $d_s < 2$ and noncompact for $d_s > 2$. Hence the average lifetime of each particle can be obtained by combining (4) and (5) with $t_{\text{el}} = \tau$ to obtain

$$\tau \sim \rho^{-1/f}. \quad (7)$$

It is now straightforward to find the exponent α from (2), with (3), (7), and (1), as

$$\alpha = f. \quad (8)$$

This result agrees with the existing and widely accepted results found by a number of other arguments.^{5,10} Clearly, the critical dimension for the reaction $A + A \rightarrow 0$ is $d_s = 2$. Note that α is dependent only on the spectral dimension d_s and is independent of the fractal dimension d_f . When $f = 1$ ($d_s > 2$), the classical kinetic results are recovered.

B. Two species: $A + B \rightarrow 0$

The d_f -independence of the reaction rate is generally believed to also be true for the $A + B \rightarrow 0$ reaction. However, in the following discussion we argue that for the two-species case the exponent α does in fact depend on the fractal dimension. In particular, we argue that the naive extension of the exponent $\alpha = d/4$, obtained for the $A + B \rightarrow 0$ reaction in d -dimensional Euclidean spaces to $\alpha = d_s/4$ in fractal spaces, is incorrect.

For the reaction $A + B \rightarrow 0$, the last term in the expression for the reaction rate shown in (2) is no longer valid since not all of the nearest neighbors are A - B pairs due to the possible formation of like-particle aggregates. Since only the particles on the surfaces of such aggregates have

the chance to react with their counterparts, the rate of reaction has to be suitably scaled down. Let Λ denote the average size of an aggregate. Then, the factor by which the reaction rate must be reduced due to the aggregation of like particles is $\Lambda^{d_f}/\Lambda^{d_f-1} = \Lambda$, which is the ratio of inactive particles to active ones, since the numerator is of the order of the volume of the aggregate, while the denominator is of the order of the surface of an aggregate. Therefore (2) should be modified to read

$$R_{AB} \sim \frac{N(1/\tau)}{\Lambda}, \quad (9)$$

with R_{AB} defined as the reaction rate for $A + B \rightarrow 0$, $R_{AB} = -d\rho_A/dt = -d\rho_B/dt$. Note that N is still defined as the number of nearest-neighbor pairs (regardless of their identity), and τ is still the time for a particle to reach a nearest neighbor (also regardless of identity). Again, for $d_s < 2$, the exploration of a random walker is known to be compact. Hence the linear size of an aggregate at time t is the same as the distance a random walker has explored in time t . With the help of (5), and with $t_{\text{el}} = t$,

$$S \sim \Lambda^{d_f} \sim t^{d_s/2} \quad \text{for } d_s < 2, \quad (10)$$

we have

$$\Lambda \sim t^{d_s/2d_f}. \quad (11)$$

Since N and τ are defined exactly as they were in the $A + A \rightarrow 0$ case, we can find the exponent α with the use of (9), (3), (6), (7), (1), and (11):

$$\alpha = \frac{d_s}{2} \left[1 - \frac{d_s}{2d_f} \right] \quad \text{for } d_s < 2, \quad (12)$$

which is dependent on the fractal dimension d_f . Consequently, if the reaction takes place on a fractal, α increases as d_f increases. Thus the relation $\alpha = d_s/4$, commonly conjectured as an extension to fractal lattices of the results for the $A + B \rightarrow 0$ reaction in Euclidean lattices, is only valid when $d_s = d_f$, which is, in turn, true *only* for Euclidean spaces. Equation (12) also shows that when $d_f \rightarrow \infty$, α becomes $d_s/2$, which is the same exponent as for $A + A \rightarrow 0$. This result can be explained directly from (11), where we see that Λ approaches the nearest-neighbor distance [i.e., $\Lambda \rightarrow 1$ in the proportionality relation (9)] when $d_f \rightarrow \infty$. This means that there is no species segregation for a fractal geometry embedded in a very high-dimensional Euclidean space. Hence the results for $A + A \rightarrow 0$ and $A + B \rightarrow 0$ in this limit are expected to be the same. Actually, an indication of the dependence of α on d_f can be seen weakly in the computer simulations of Zumofen, Blumen, and Klafter,¹⁵ where the deviation of the value of α from $d_s/4$ increases as the Euclidean dimension of the space in which their Sierpinski gasket is embedded increases. The dependence of α on d_f can be seen more clearly in the simulations of Meakin and Stanley¹⁶ on percolation clusters embedded in Euclidean spaces of dimension $d = 2$ and $d = 3$. Although d_s is always $\frac{4}{3}$ for percolation fractals in any dimension, α for $d = 3$ ($d_f = 2.5$) is larger than for $d = 2$ ($d_f = 1.9$),

which is in agreement with the prediction (12). Although these simulations are indicative of the behavior that we predict, more careful simulations are needed to examine the dependence of α on d_f .

Consider now the reaction $A + B \rightarrow 0$ on a fractal with $d_s > 2$. Since f in Eq. (5) is now unity and since a random walk on such a fractal is no longer compact, we expect that

$$\Lambda \leq t^{1/d_f}. \quad (13)$$

Unfortunately, we know of no derivation of the actual form of Λ , nor have we been able to produce one ourselves. We might conjecture a form that obeys the following requirements: It must satisfy the inequality (13), it must be continuous at $d_s = 2$, and the exponent α must be equal to $d/4$ for Euclidean spaces ($d_s = d_f = d$) when $d < 4$. A simple form that satisfies all these requirements is

$$\Lambda \sim \begin{cases} t^{\frac{1}{2}(1+d_s/d_f-d_s/2)} & \text{for } 2 \leq d_s < \frac{2d_f}{d_f-2}, \\ 1 & \text{for } d_s > \frac{2d_f}{d_f-2}, \end{cases} \quad (14)$$

where the cutoff $2d_f/(d_f-2)$ is determined by the requirement of positivity of the exponent. With (9), (3), (6), (7), and (14), it is found that

$$\alpha = \begin{cases} \frac{1}{2} - \frac{d_s}{2d_f} + \frac{d_s}{4} & \text{for } 2 \leq d_s < \frac{2d_f}{d_f-2}, \\ 1 & \text{for } d_s > \frac{2d_f}{d_f-2}. \end{cases} \quad (15)$$

With this expression we recover the known behavior for Euclidean spaces with the appropriate critical dimension 4. In general, however, our conjecture (and most any reasonable conjecture) again leads to a dependence of the decay rate of the density on the fractal dimension d_f and not only on the spectral dimension d_s . If $d_f \rightarrow \infty$, we recover the classical result $\alpha = 1$ for $d_s \geq 2$, and the critical dimension is then 2 and not 4. In general, the critical spectral dimension for transition from "anomalous" to classical behavior is $2d_f/(d_f-2)$. To our knowledge, the dependence of the critical spectral dimension on the fractal dimension has not been previously reported. Again, more simulations are needed to verify these results.

We stress that, whereas the $d_s > 2$ results are based on a conjecture, those for $d_s \leq 2$ are rigorous. These latter results also lead to a decay of the densities that depends on both d_f and d_s , a dependence that has not been previously noted.

III. WITH SOURCES: STEADY STATE

In the presence of sources that continue to feed reactants into the system as time goes on, a steady state can be established at long times. It is this steady state that we now characterize. We assume that the sources are spa-

tially and temporally random and, in the case of the $A + B \rightarrow 0$ reaction, that there are no correlations between the A 's and B 's as they are injected into the system (but that their total numbers are equal at all times). Thus, in language that we have used in the past, the sources are strictly conservative but uncorrelated.

A. Single species: $A + A \rightarrow 0$

Since the steady state involves no time-dependent quantities, the rate of reaction should here be expressed directly in terms of ρ . The reaction must be balanced by the particle input for a steady state to be established.

The reaction rate is, as before, controlled by the lifetime of each particle and by the number of nearest-neighbor pairs of particles in the system, so that we can still write, as in (2),

$$R_{AA} \sim N \frac{1}{\tau}. \quad (16)$$

The connections between the particle density and the particle lifetime obtained in the absence of sources are still valid in their presence (albeit that ρ is now a constant in time). Therefore we can use (3) and (7) in (16) to obtain the rate equation

$$R_{AA} \sim \rho^{1+1/f}, \quad (17)$$

with f given in Eq. (6). This reaction rate must be balanced with the rate R of input of A particles into the system, i.e., $R \sim R_{AA}$. Therefore

$$R \sim \begin{cases} \rho^{1+2/d_s} & \text{for } d_s < 2, \\ \rho^2 & \text{for } d_s > 2. \end{cases} \quad (18)$$

This result has been found using a number of other methods.^{8,11} The critical dimension for nonclassical behavior is 2.

We note that the rate law (17) is identical to that obtained in the asymptotic analysis of Sec. II: Indeed, if in (2) we rewrite $t^{-\alpha-1}$ in terms of ρ using (1), then with (8) we obtain the rate law (17). That the rate law is the same in the asymptotic regime without sources and in the steady state with sources would seem to indicate that the spatial distribution of reactants in both cases is essentially the same. This equality is by no means self-evident *a priori*, since the random sources do not reflect this pattern. Furthermore, this behavior is quite different than that of the $A + B \rightarrow 0$ case, where the spatial patterns of reactants in the presence and absence of sources are not the same.

B. Two species: $A + B \rightarrow 0$

Although the rate of reaction is still given by (9), and this rate must again be equal to the rate at which the reactants are introduced in the system, this observation is not particularly useful unless we know the relation between the size Λ of the aggregate and the density of particles. In the absence of sources, we were able to establish this relation for $d_s \leq 2$ and conjecture it for $d_s > 2$; but it

is more difficult to do either one of them *a priori* in the presence of sources. We therefore need an alternative point of departure. We observe that relation (7), between the particle density and the time for a particle to reach one of its nearest neighbors (regardless of identity), is still valid.

Let us first consider the situation of a relatively high initial density (cf. below) of reactants, so that the injected particles fall on or very near a particle in the medium. In the parlance of our previous work, this might be considered close to the case of "vertical annihilation," although the latter is strictly defined only when the finite size of the reacting particles is taken into account. The sources of *A* and *B* particles would have little effect on the densities if the numbers of injected *A* and *B* particles were *locally* equal ("tightly correlated source"): For every injected *A* particle that reacts with a *B* particle, a new *B* particle would also be injected in the same locality. Similarly, for every injected *B* particle that reacts with an *A* particle, a new *A* particle is deposited in the same locality. In this scenario the sources would thus cause essentially no changes in particle densities, and all the changes would come about exclusively as a result of the chemical reaction. The densities would then necessarily decrease with time. Once the density is sufficiently low for the above picture to break down because of large regions devoid of reactants, the sources, although tightly correlated, can begin to have an effect on the densities. A balance between the effects of the sources and the chemical reaction then becomes possible, and a low-density steady state can be established. A steady state involving higher densities can only come about if there are local fluctuations in the relative numbers of injected *A* and *B* particles (while preserving their global equality). The local excess of one or the other of the particles can cause local buildups of the density that can be exactly balanced by the chemical reaction and can therefore lead to a steady state.

These latter remarks can be quantified. The fluctuations in the local densities for uncorrelated spatially random sources are of the order of the square root of the injection rate, \sqrt{R} . These fluctuations must be balanced by the chemical reaction. The reaction occurs only at "interfaces" where *A* particles and *B* particles are in contact; i.e., they do not occur inside of aggregates of a single species. The rate of reaction is therefore proportional to the inverse of the time τ that it takes a particle to reach a nearest neighbor (the same quantity introduced earlier) times a factor that we call *C*, which measures the "interface area" between aggregates along which the reaction can occur. In a Euclidean geometry and in some fractal geometries, if there are macroscopic aggregates, then *C* may depend on the size of the system. In a Sierpinski gasket, *C* is $O(1)$, even if there is macroscopic segregation, because reactions can only occur at isolated points of the fractal, where one segregated aggregate meets another.^{1,9} If there is no segregation, then *C* is of the order of the coordination number. In any case, *C* is essentially independent of the steady-state density provided that the density is not too low (cf. below). The steady-state balance is embodied in the relation

$$\sqrt{R} \sim c \frac{1}{\tau}, \quad (19)$$

from which, with (7), it immediately follows that

$$R \sim \begin{cases} \rho^{4/d_s} & \text{for } d_s < 2, \\ \rho^2 & \text{for } d_s > 2, \end{cases} \quad (20)$$

which agrees with the recent findings of Clement, Sander, and Kopelman.⁶⁻⁸ Note that the critical dimension is again 2. The result (20) has recently been verified via simulations on a two-dimensional Sierpinski gasket.¹⁷

In our discussion we introduced the caveat of a steady-state density that is not too low. The caveat is introduced for two reasons. The first is that, at low densities, injection no longer involves only vertical annihilation, and one must therefore consider the possibility that even tightly correlated sources can affect the problem in that they can introduce new interfaces. The second concerns the factor *C*, which may become density dependent if the density is very low, because the number of nearest-neighbor molecules increases (albeit the distance to each also increases, as reflected in τ). In this case the rate law will deviate from the result (20), and the deviation may include the fractal dimension d_f , as well as the spectral dimension d_s . Such a deviation at very low steady-state densities would be consistent with the fact that the critical dimension for classical behavior in the absence of sources is 4, while in the presence of sources Eq. (20) gives a critical dimension of 2. It is possible that the critical dimension itself depends on d_s and/or d_f with decreasing density. Note that during the decay of the density toward a low steady-state value, the system is expected to behave as though there were no sources (and therefore "anomalously" up to dimension 4) until a crossover time, at which time the results with sources take over. This crossover time gets longer with decreasing steady-state density. In practice, it is very difficult to achieve very low steady-state densities in numerical simulations: The power-law relation (20), between the steady-state density and the injection rate, indicates why any numerically reasonable injection rate might lead to densities that are relatively high. All simulations that we are aware of are probably in the "high-density" regime for the purposes of this discussion and, therefore, may not be able to address possible deviations from the commonly accepted result (20).¹⁸ Low-density steady states in the absence of vertical annihilation have been discussed in Refs. 7 and 8.

IV. CONCLUSIONS

We have used scaling arguments involving the particle density, the time for a particle to reach a nearest neighbor, and the size of segregated aggregates, where appropriate, to study diffusion-limited reactions of the form $A + A \rightarrow 0$ and $A + B \rightarrow 0$. Our method can deal with "big bang" reactions (no sources beyond the initial reactants) as well as "batch reactions" (sources that continually inject reactants). For the $A + A \rightarrow 0$ reaction, in both cases we obtain results for the rate law, the steady-

state density, and the critical dimensions for anomalous behavior that agree with those found earlier by other methods. For $A + B \rightarrow 0$, however, our results deviate from those of others. In particular, in the absence of sources, we find a rate law that depends not only on the spectral dimension but also on the fractal dimension. We observe that existing simulations contain indications of this behavior, but have not been specifically designed to address the question. It would be useful to carry out simulations in a series of systems of similar spectral dimension but differing fractal dimension (or vice versa). In the presence of sources, we present arguments that in-

dicating a possible deviation from the accepted steady-state results (and again a possible dependence on the fractal dimension) when the steady-state density is very low. Existing simulations probably do not probe sufficiently low steady-state densities to be affected by these deviations.

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