Reaction kinetics on fractals: Random-walker simulations and exciton experiments

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Both computer simulations and laboratory experiments on binary reactions of random walkers on fractal spaces bear out a recent conjecture: The time development of the reaction is dominated by the intrinsic fractal (fracton, spectral) dimension. For the Sierpinski gasket the effective spectral dimension for reactions is $d_s' = 1.38$ (actual spectral dimension $d_s = 1.365$). For the percolating cluster (60%, square lattice) $d_s' = 1.34$ ($d_s = 1.333$). From the exciton percolation laboratory experiments $d_s' = 1.5$, based on triplet-triplet annihilation in naphthalene isotopic mixed crystals at 2 K.

Within the last year, intrinsic dynamical properties of fractals, e.g., random walk, conductivity, phonon, and magnon effects, have been related to an unexpected new dimension d_s—the spectral (fracton) dimension.[1-4] For Euclidean (three-dimensional) spaces the classical behavior is retained, giving the classical diffusion constant, the Debye (T^3) heat capacity at low temperatures, and Ohm's law. For fractal spaces the spectral dimension leads to drastic deviations from the classical laws. It has also been conjectured that the binary reaction coefficient is related to the same spectral dimension to which the magnon and phonon densities of states are related.[5] Our simulations bear this out for both a deterministic fractal (Sierpinski gasket) and a random one (percolating cluster). Our fusion experiments on naphthalene isotopic mixed crystals exhibit the same nonclassical behavior, at and below the empirical "percolation concentration."[6]

We discuss binary reactions with one kind of reactant:

$$A + A \rightarrow \text{products} \ , \tag{1}$$

where the A species are random walkers. The standard, classical, second-order rate law gives

$$\frac{-d\rho}{dt} \propto \rho^2 \ , \tag{2}$$

where ρ is the density of walkers.

However, in microscopically heterogeneous media (we include low-dimensional spaces as special representatives of heterogeneous three-dimensional spaces), one may get

$$\frac{-d\rho}{dt} \propto t^{-h}\rho^2 \ , \tag{3}$$

which is equivalent to a time-dependent rate coefficient.[7] We have conjectured[5] that for fractal (self-similar) spaces h is related to an *effective* spectral (fracton) dimension[8] d_s' (we use the prime to distinguish this reaction exponent from the conventional d_s):

$$h = 1 - d_s'/2 \ . \tag{4}$$

It follows from Eq. (3) that the integrated rate equation is

$$\rho^{-1} - \rho_0^{-1} \propto t^{1-h} \ . \tag{5}$$

Our Monte Carlo simulations[9] are for the reaction

$$A + A \rightarrow A \ . \tag{6}$$

No "traps" are present in these systems and all walkers move independently (one at a time). When two walkers occupy the same site within one instant, one walker is removed from the system and the other walker continues its walk unperturbed. This is the only type of walker interaction allowed.

The planar Sierpinski gasket was generated iteratively using a method similar to Pascal's triangle. An eighth-order Sierpinski gasket was used consisting of approximately 10 000 sites where we defined a site as the vertex of a triangle. If a walker is at one of the three corners of the largest triangle it remains confined to the finite gasket, and its subsequent move is restricted to only one of its two possible nearest-neighbor sites. At time $t = 0$, walkers were started at random sites on the gasket. We performed our reacting random-walker simulations with an initial walker density of $\rho_0 = 0.1$; 500 runs were performed.

Simulations on the percolating cluster started with an initial walker density of $\rho_0 \simeq 0.02$ on a 60% occupied lattice. These simulations used 400×400 *square* lattices and consisted of 25 runs, each for a different lattice realization. Periodic boundary conditions were imposed on these lattices.

The Michigan terminal system uniform random-number generator (FUNIF) was used in all simulations on the percolating cluster and on the Sierpinski gasket. A linear least-squares regression was used to obtain values for $1 - h$ in Eqs. (3) and (5). Each walk was followed for 2000–4000 steps.

The laboratory experiments on molecular exciton kinetics consisted of monitoring the evolution in time of the delayed fluorescence and phosphorescence resulting from the homofusion (annihilation) of Frenkel triplet excitons on percolation clusters in an isotopic alloy crystal, naphthalene-h_8 in naphthalene-d_8, at a temperature of 2 K. Further details are given in Refs. 5–7, 10, and 11.

Table I gives the results obtained from a linear regression on the simulation data of Fig. 1 in the long-time limit. These are compared with single random-walker simulation results and asymptotic theories, obtained from[2] the mean number of distinct sites visited:

$$S(t) \propto t^{1-h} \ . \tag{7}$$

The single random-walker simulations (this work and Refs. 8 and 12) were performed for lattice sizes and times similar to those of the reacting walkers.

The results of Table I appear to substantiate the conjecture that the effective spectral dimension of the reacting

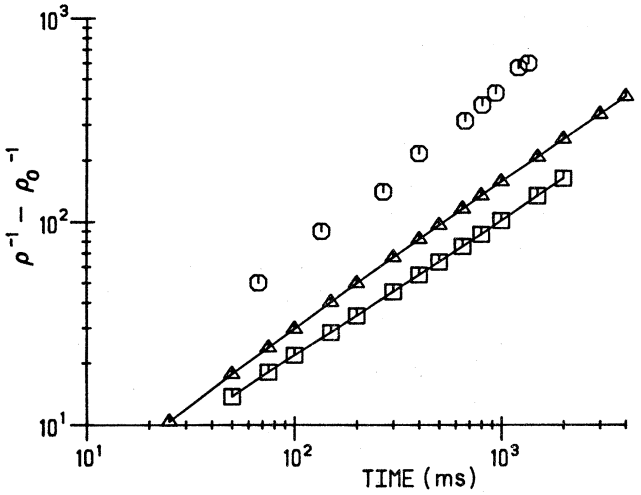

FIG. 1. Reacting random walkers. Bottom: On a square-lattice (60%) infinite percolation cluster ($\rho_0 \simeq 0.02$). Middle: On a triangular Sierpinski gasket ($\rho_0 = 0.1$). Top: Triplet excitons on a long-range cluster of naphthalene (8%) in a naphthalene-d_8 crystal (ρ_0 normalized to 5×10^{-3}). Time in ms.

walkers is the same as that of the single walker on both the *Sierpinski gasket* and the *percolating cluster*. We note that the correlation length of the 60% percolating cluster is long enough[8] to give the same fracton dimension as the incipient percolating cluster[8,13-15] (59.31%). Preliminary data[16] on the three-dimensional Sierpinski gasket[4] substantiate the same conjecture ($d_s = 1.547$, $d_s' = 1.56$).

The laboratory experiments represent a long-range percolation case where the effective critical concentration[10] is about 7% and the effective topology is that of a square lattice.[6,7,10] The Fig. 1 results for the experimental data are based on triplet exciton density measurements, i.e., only phosphorescence measurements. This gives $1-h = 0.82 \pm 0.05$. A related treatment based on Eq. (3) requires both phosphorescence and delayed fluorescence measurements [see Ref. 5(a)]. It gives $h = 0.28 \pm 0.05$ (for earlier times).

TABLE I. Effective spectral dimensions $d_s'/2$.

	Reacting walkers (Asymptotic)	Single walkers Simulation	Single walkers Theory[a]
Sierpinski	0.69	0.69[b]	0.682
Percolation cluster	0.67	0.67[c]	0.667

[a] Reference 4.
[b] 0.686 in Ref. 12.
[c] Reference 8.

The effective spectral density is thus $d_s' = 1.5 \pm 0.1$. Considering that this 8% sample may be significantly above the critical long-range percolation concentration, the above value is consistent with d_s' values found in Ref. 8, for lattices above the critical concentration, i.e., with a crossover to Euclidean behavior. We note that for crossover cases d_s' is a crude effective fracton dimension as the asymptotic behavior is really Euclidean. Such crossovers, for single and reacting random walkers, are discussed elsewhere.[17] Actually, the experimental data appear to follow the fractal slopes at early times but to "cross over" to Euclidean at later times.

In conclusion, the conjecture that fracton exponents apply to binary reactions of random walkers is borne out by simulations on both deterministic and random fractals. This may be of much relevance to reactions in microscopically heterogeneous media. Our experimental results for molecular exciton reactions illustrate this point.

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