FRACTAL TO CLASSICAL CROSSOVER OF CHEMICAL REACTIONS *

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Computer simulations on binary reactions of random walkers (A + A → A) on two- and three-dimensional percolation clusters bear out the recent superuniversality conjecture (integrated reaction rate $\propto t^{2/3}$). Moreover, the fractal-to-euclidean crossover ($t^{2/3}$ to t dependence) parallels that of the single walker.

1. Introduction

There has been much recent interest in the fractal aspects of heterogeneous chemical reactions [1–6]. While most work considered the trapping rate of excitons or electrons at impurity or defect centers [1–4], i.e. where only one reactant moves (the "trap" is fixed) there has also been some specific work on binary chemical reactions where both reactants are free to move, i.e. genuine bimolecular reactions [5–7]. For the simplest such reaction,

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

it has been shown via simulation [6] (confirming an earlier conjecture [5]) that the reaction of eq. (1), when proceeding on a fractal matrix, obeys the following integrated rate equation:

$$\rho^{-1}(t) - \rho^{-1}(0) = K_0 t^f, \tag{2}$$

where $\rho(t)$ is the reactant density at time t, K_0 a constant and

$$f = \tfrac{1}{2} d_s \tag{3}$$

where d_s is the *spectral dimension* ("fracton" dimension) [8]. For a euclidean lattice (homogeneous medium), $d_s = 2$, i.e. $f = 1$, and eq. (2) reduces to the classical (textbook) result:

$$\rho^{-1}(t) - \rho^{-1}(0) = K_0 t. \tag{4}$$

Eq. (4) tells us that the *rarefication of the reactant species A* (described by the left-hand side) *proceeds linearly in time.* However, for disordered media of fractal nature, eq. (2) tells us that this rarefication proceeds with a fractal power of the time, prescribed by the spectral dimension of the fractal.

Experimental results for exciton fusion (triplet–triplet annihilation: T + T → products) on binary lattices [5,6,9] have shown a behavior obeying eq. (2), and *not* eq. (4), under appropriate conditions (in refs. [5,9] the differential rate equation leading to eq. (2) has been used). However, microscopically disordered media, such as random binary lattices, have an exact fractal nature [8,10] only under very restricted conditions, i.e. at the critical percolation concentration C_c. The question then arises: How widely spread and important is the fractal regime for chemical reactions. The present work supplies some quantitative answers and shows that the regime of fractal behavior is not limited to some exotically restricted conditions.

The logical premise here (as in ref. [5]) has been that the reaction in a system of identical random walkers (A) will reflect the motion of a single random walker: The same power f that determines the exploration range $S(t)$ of a single random walker,

$$S(t) \propto t^f, \tag{5}$$

will also determine the reaction kinetics (e.g. eq. (2)). We note that, on a discrete lattice or matrix, $S(t)$ re-

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duces to $S(N)$, the mean number of distinct sites visited in N steps:

$$S(N) \propto N^f. \qquad (5')$$

The conjecture that f is given by the spectral dimension d_s (eq. (3)) [8,10] has been confirmed by many simulations [11]. For percolation lattices this conjecture only holds [8–11] at the percolation threshold (C_c). It has, however, been conjectured that there exists a *crossover* from fractal to euclidean behavior that is related to the percolation correlation length (ξ) [4,12]. This crossover can be crudely expressed [11] by letting the exponent f vary from *2/3* (the magic value at percolation thresholds in all dimensions [8]) to *unity* (the value for three-dimensional lattices and continua). Here we give quantitative simulation results for the *single random walker crossovers*. We then show that the *crossovers of reacting systems of random walkers* are completely analogous (i.e. the dependence of f on the concentration and on the time).

2. Simulations and results

The methods of the Monte Carlo simulations have been described before [6,11,13,14]. Figs. 1 and 2 show the *single-walker exploration* versus time for square (two-dimensional) and simple cubic (three-dimensional) lattices, respectively. In each case the low-

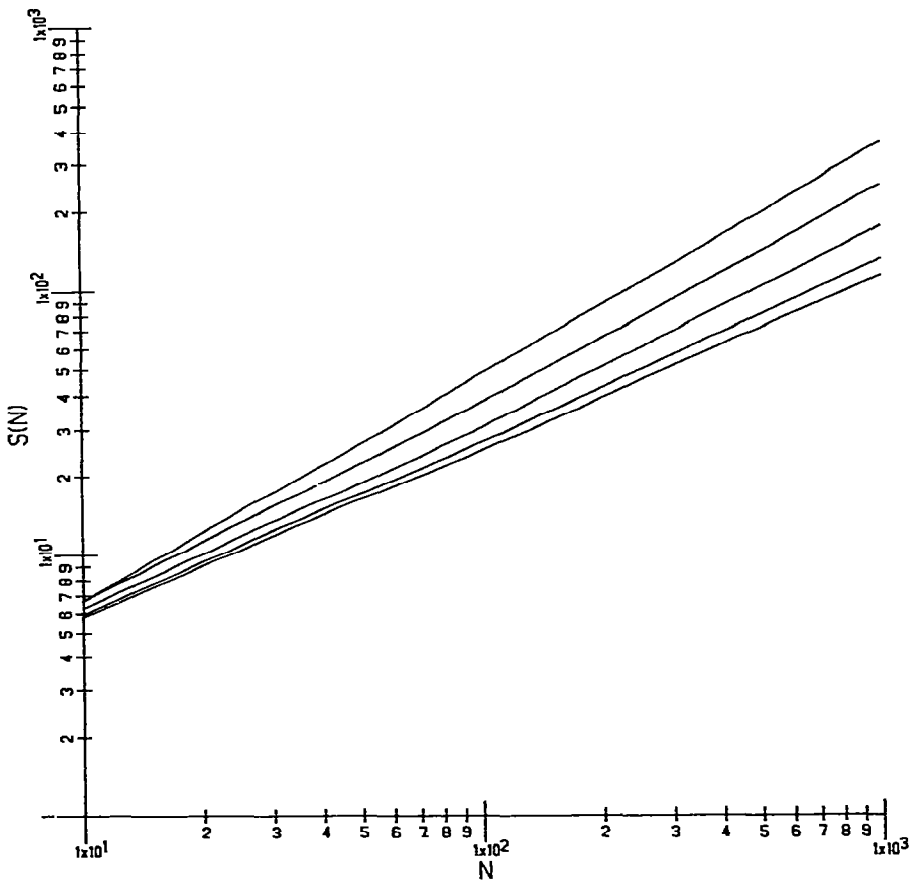


Fig. 1. S_N versus N for a two-dimensional square lattice. Top to bottom: C = 1.00, 0.80, 0.70, 0.65, and 0.60. Averages of 1000 runs, except for the 0.60 case where 2290 runs were retained out of 3283 runs, in order to discard the walks on finite clusters [11, 13].

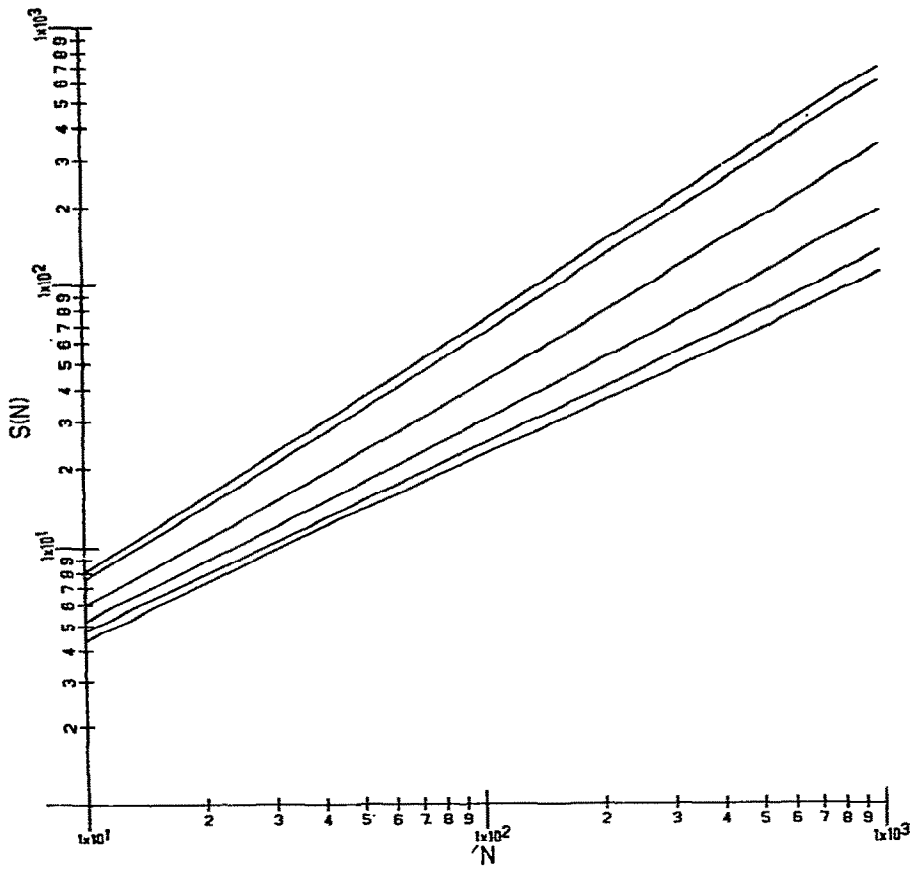


Fig. 2. S_N versus N for a three-dimensional simple cubic lattice. Top to bottom: C = 1.00, 0.80, 0.50, 0.40, 0.36 and 0.32. Averages of 1000 runs except for the 0.32 case where 501 runs were retained out of 1000, in order to discard the walks on finite clusters [11,13].

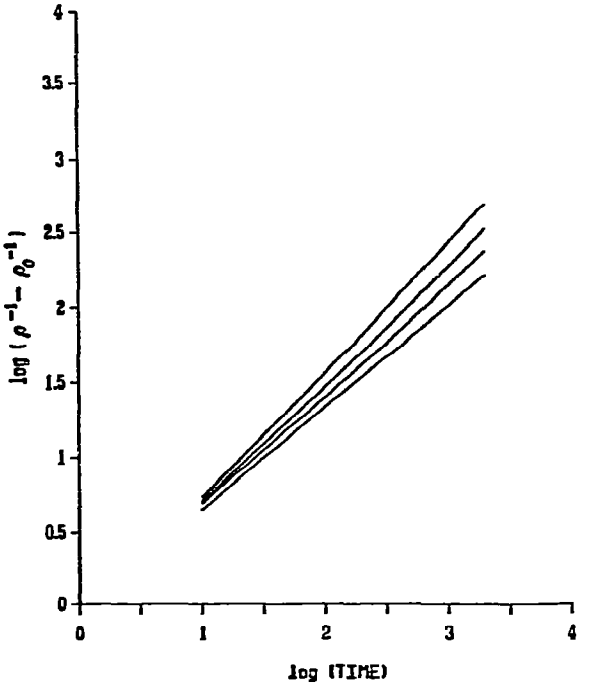
est curve is close to the threshold (critical concentration C_c) and the higher curves are for higher concentrations, up to unity (pure crystal). On both figures the lowest curves are quite straight and have a slope close to 2/3. The highest curve for the three-dimensional case (C = 1.0) is also fairly straight, with a slope close to unity (only the three-dimensional case should have a slope of strictly unity, and this only at $t \to \infty$, because of the logarithmic correction involved in the two-dimensional random walk [15]). We would particularly like to emphasize that the lines for the intermediate concentrations are curved, not straight. For this regime, at early times, the slope is lower, closer to the fractal value (2/3) while at longer times it is higher, close to the euclidean value (1). Note that all "crossover" lines curve in the "upward" direction. A quantitative crossover description, in terms of effective f values, is given in table 1.

Figs. 3 and 4 show the *reacting walker rarefication* versus time, again for square (two-dimensional) and simple cubic (three-dimensional) lattices, respectively. The behavior is very similar to that mentioned for the single walker. The lowest curves (at about C_c), show straight lines with slopes very close to 2/3 (see table 1 for exact values), while the highest curves show, again, fairly straight lines with slopes close to unity (especially for the three-dimensional case). Again, the curves for the intermediate concentrations show a "crossover" from lower (about 2/3) to higher (below 1) values, and again these lines curve in the

Table 1
Effective f values

C	Single walker		Reacting walkers	
	two-dim. (slopes from fig. 1)		two-dim. (slopes from fig. 3)	
	overall f	asymptotic f	overall f	asymptotic f
1.00	0.889	0.883	0.920 [a]	0.935 [a]
0.80	0.839	0.822	0.865	0.866
0.70	0.768	0.785	0.806	0.831
0.65	0.713	0.722	0.748	0.780
0.60	0.665	0.671	0.676	0.674
	three-dim. (slopes from fig. 2)		three-dim. (slopes from fig. 4)	
	overall f	asymptotic f	overall f	asymptotic f
1.00	0.988	0.989	0.981	0.980
0.80	0.981	0.987	0.976	0.967
0.70			0.970	0.980
0.50	0.935	0.945	0.941	0.961
0.40	0.850	0.863	0.861	0.912
0.36	0.757	0.786	0.748 [b]	0.763 [b]
0.32	0.709	0.677	0.674	0.687

[a] Ref. [16]. [b] $C = 0.35$.



"upward" direction. A quantitative crossover description is given in table 1, columns 4 and 5. This compares very favorably with table 1, colums 2 and 3, for the single walks.

3. Summary

Evidently there is a very satisfactory analogy between the single and the reacting multiple random walk systems. This bears out earlier conjectures [5,6] and demonstrates the usefulness of the concept of *fractal rate constant and fractal-to-classical crossover.* Most striking, perhaps, is the fact that for the system of reacting random walkers, we find $f = 0.67$ for the two-dimensional case and 0.69 for the three-dimen-

◄ Fig. 3. $\mathrm{Log}[\langle\rho^{-1}(t)\rangle - \langle\rho^{-1}(0)\rangle]$ versus $\log t$ for a two-dimensional square lattice. Top to bottom: $C = 0.80, 0.70, 0.65, 0.60$. Averages of 100 runs, 2000 steps each, on 200 × 200 lattices, with cyclic boundary conditions, $\rho(0) = 0.02$. Forced random walks, limited to largest cluster only.

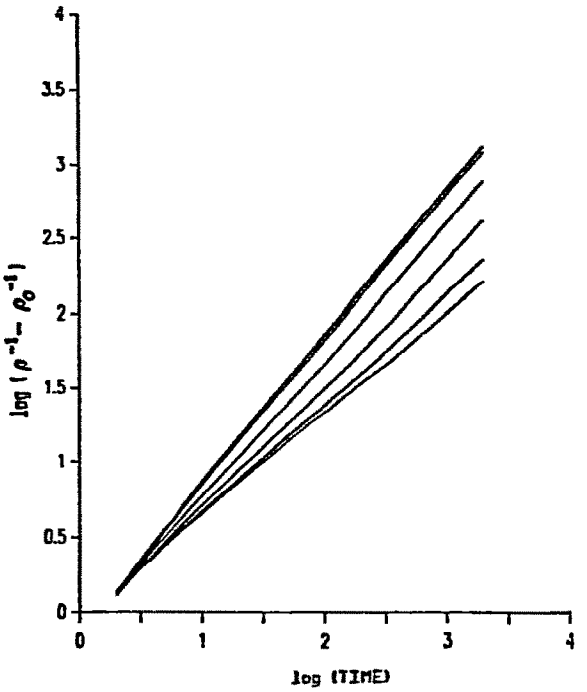


Fig. 4. Log $[\langle \rho^{-1}(t) \rangle - \langle \rho^{-1}(0) \rangle]$ versus log t for a three-dimensional simple cubic lattice. Top to bottom: $C = 1.00, 0.80, 0.50, 0.40, 0.35, 0.32$. Averages of 1000 runs, 2000 steps each, on 40 X 40 X 40 lattices, with cyclic boundary conditions, $\rho(0) = 0.02$. Forced random walks, limited to largest clusters only.

sionl case, in excellent agreement with the single random walker result of $f = 0.67$ and 0.68, respectively, and the superuniversality conjecture of 2/3.

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