

Fractal chemical kinetics: Simulations and experiments

L. W. Anacker and R. Kopelman

Citation: *The Journal of Chemical Physics* **81**, 6402 (1984); doi: 10.1063/1.447553

View online: <http://dx.doi.org/10.1063/1.447553>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/81/12?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Timeparallel Simulation of Stochastic Chemical Kinetics](#)

AIP Conf. Proc. **1048**, 174 (2008); 10.1063/1.2990884

[Efficient binomial leap method for simulating chemical kinetics](#)

J. Chem. Phys. **126**, 224109 (2007); 10.1063/1.2741252

[Binomial leap methods for simulating stochastic chemical kinetics](#)

J. Chem. Phys. **121**, 10356 (2004); 10.1063/1.1810475

[Fractal kinetics and surface reactions](#)

J. Chem. Phys. **108**, 4572 (1998); 10.1063/1.475868

[Kinetic simulation of a plasma collision experiment](#)

Phys. Fluids B **5**, 2816 (1993); 10.1063/1.860670



siderable information on the potential surfaces involved.

We thank Mark Dyer for assistance with the lasers, and Jay Jeffries for many useful discussions. This research was supported by the National Aeronautics and Space Administration.

¹S. Green and R. N. Zare, *Chem. Phys.* **7**, 62 (1975).

²R. N. Dixon and D. Field, *Proc. R. Soc. A* **368** 99 (1979).

³M. H. Alexander, *J. Chem. Phys.* **76**, 5974 (1982).

⁴T. Orlikowski and M. H. Alexander, *J. Chem. Phys.* **79**, 6006 (1983).

⁵P. Andresen, G. S. Ondrey, B. Titz, and E. W. Rothe, *J. Chem. Phys.* **80**, 2548 (1984).

⁶R. Vasudev, R. N. Zare, and R. N. Dixon, *J. Chem. Phys.* **80**, 4863 (1984).

⁷K. Kleinermanns and J. Wolfrum, *J. Chem. Phys.* **80**, 1446 (1984).

⁸P. Andresen, D. Häusler, and H. W. Lülf, *J. Chem. Phys.* **81**, 571 (1984).

⁹D. P. Dewangan and D. R. Flower, *J. Phys. B* **14**, 2179 (1981); **16**, 2157 (1983).

¹⁰J. D. Bradshaw, M. O. Rodgers, and D. D. Davis, *Appl. Opt.* **23**, 2134 (1984).

¹¹A. S. Sudbø and M. M. T. Loy, *J. Chem. Phys.* **76**, 3646 (1982).

¹²R. A. Copeland and D. R. Crosley, *Chem. Phys. Lett.* **107**, 295 (1984).

¹³J. A. Coxon, *Can. J. Phys.* **58**, 933 (1980).

¹⁴J. P. Maillard, J. Chaiville, and A. W. Mantz, *J. Mol. Spectrosc.* **63**, 120 (1976).

¹⁵P. W. Fairchild, G. P. Smith, and D. R. Crosley, *J. Chem. Phys.* **79**, 1795 (1983).

¹⁶R. A. Copeland, M. J. Dyer, and D. R. Crosley, *J. Chem. Phys.* (to be published).

¹⁷M. H. Alexander and T. Orlikowski, *J. Chem. Phys.* **80**, 1506 (1984).

¹⁸T. Orlikowski and M. H. Alexander, *J. Chem. Phys.* **80**, 4133 (1984).

Fractal chemical kinetics: Simulations and experiments^a

L. W. Anacker and R. Kopelman

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

(Received 16 August 1984; accepted 1 November 1984)

An important class of heterogeneous chemical reactions occurs on or inside media that may have fractal structures. Examples are porous glasses,¹ diffusion-limited aggregates² and percolation clusters.³ Diffusion in or on such media is anomalous³⁻⁹ and so are diffusion-limited chemical reactions.¹⁰⁻²² What are the rules for transient and steady state reactions on such media? It has been shown experimentally^{12,13} that an elementary reaction



may have a reaction rate (ρ = density of species A, t = time):

$$-d\rho/dt = k\rho^X \quad X \geq 2, \quad (2)$$

where the power ("order") X may be much larger than 2. We present here a simple argument, relating X to the fractal dimension of random walks in a heterogeneous medium.^{6-9,23} For a spectral dimension $d_s < 2$ we find $X = 1 + 2/d_s$. An amusing special case is a linear lattice, for which $X = 3$. The scaling result is validated by a very large scale Monte Carlo simulation on a supercomputer and by experimental results.

The random walker's exploration space S ("mean number of distinct sites visited") is given by

$$S \propto t^f \quad 0 \leq f \leq 1 \quad (t \rightarrow \infty), \quad (3)$$

where $f = 1$ for classical (3D homogeneous) diffusion and $f < 1$ for anomalous diffusion.⁶⁻⁹ It has been shown²⁴ for the fractal exponent f that $f = d_s/2$ for $d_s < 2$. It has also been shown^{14,18,21} that the rate for the simple binary reaction (1) is

$$-d\rho/dt = k_0 t^{-h} \rho^2 \quad 1 > h \geq 0 \quad (t \rightarrow \infty), \quad (4)$$

where the heterogeneity exponent h is related to the fractal exponent f . For the simple binary reaction of Eq. (1), $h = 1 - f$. This has been verified by extensive simulations.^{21,22,25,26} The integrated rate equation, obtained from Eq. (4), is

$$\rho^{-1} - \rho_0^{-1} = k_0 f^{-1} t^f \quad (\text{if } h = 1 - f), \quad (5)$$

where $\rho_0 \equiv \rho(t=0)$. Hence,^{14,20}

$$t = (k_0^{-1} f)^{1/f} \rho^{-1/f} \quad t \rightarrow \infty \text{ or } \rho \rightarrow 0. \quad (5')$$

A simple substitution of Eq. (5') into Eq. (4) gives ($k \equiv k_0^{1/f} f^{1-1/f}$):

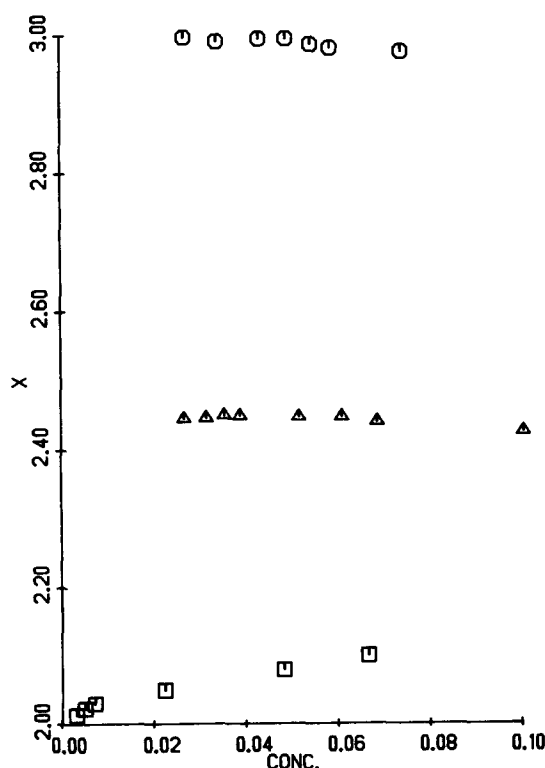


FIG. 1. Effective reaction order X vs the mean steady state walker density, $\text{CONC.} \equiv \langle \rho_{ss} \rangle \propto R^X$. Top to bottom: 1D lattice (10^4 – 10^5 sites), planar Sierpinski gasket ($\sim 10^4$ sites), and 3D simple cubic lattice (64^3 sites). Steady states are achieved well below 10^4 steps.

$$-dp/dt = kp^{1+1/f} \quad t \rightarrow \infty. \quad (6)$$

This gives an elementary reaction order X :

$$X = \frac{2-h}{1-h} = 1 + f^{-1} \quad (7)$$

and relates X to the effective spectral dimension²³⁻²⁷ of the medium. Obviously, for the case of $h = 0$ ($f = 1$), the classical result, $X = 2$, is regained.

The above relation [Eq. (7)] is new. However, for *transient* reactions it is implicit in Eqs. (4) and (5). The latter have been tested by simulations^{21,25,26} on both Sierpinski gaskets ($f = 0.68$) and percolating clusters ($f \cong 2/3$). We thus expect X to be 2.46 for the Sierpinski gasket and 2.50 for percolating clusters (except, possibly, 2.53 for 2D percolating clusters^{8,27}). A special case is the 1D lattice ($f = 0.5$), where we expect $X = 3$ (three!).

Experiments were done for the exciton fusion reaction on percolating naphthalene clusters.¹² For the critical percolation concentration (8%), Fig. 2 of Ref. 12 gives a slope X of 2.5 ± 0.3 , in excellent agreement with the theory ($X = 2.5$) and the measured^{21,28} $h = 0.36$ (giving $X = 2.6$). Moreover, below percolation, the experiments^{14,18} give $h \cong 0.5$, corresponding to $X \cong 3$, while Fig. 2 of Ref. 12 gives $X \cong 3.5 \pm 0.5$. [Note, the log (fluorescence) vs log (phosphorescence) curve for the 4% sample is not straight; this is expected well below percolation.]

The above tests on Eq. (7) involved *transient* kinetics. Does Eq. (7) also hold for *steady state* kinetics? Extensive Monte Carlo simulations (Fig. 1) show that it does. In the low density limit, the cubic lattice binary reaction (Fig. 1) behaves classically, $X = 2$, while the Sierpinski gasket behaves "fractally," $X = 2.45$, and the linear lattice indeed gives $X = 3$. This is a striking demonstration of the validity of Eq. (7) for *steady state* reaction rates.²⁹ The high density trends will be discussed elsewhere. We note that two walkers occupying the same site at the same instant in time *fuse* ($A + A \rightarrow A$) and that walkers are placed on the lattice at a constant rate R .

The Cyber 205 supercomputer (Colorado State) was used for the eighth order Sierpinski gasket (100 runs for each R) and the simple cubic lattice (20 runs for $R < 5$ and 5–10 runs for larger R). The uniform pseudorandom number generator RANF was used. The University of Michigan Amdahl 5860 was used for the 1D lattice simulations (about 5 runs for each R), using the pseudorandom number generator FUNIF. Nonlinear regressions were performed to obtain the X values for Fig. 1.

The classical, diffusion-limited Smoluchowski–Noyes chemical kinetics is based on classical diffusion equations.³⁰⁻³³ An extension to fractal-like media, where the diffusion is anomalous (no diffusion constant) requires a consi-

deration of three different dimensions (Euclidean, fractal, and spectral^{6,24}). A first step in this direction has now been achieved. Generalizations to

pseudounary ($A + B \rightarrow B + \text{products}$),

binary ($A + B \rightarrow \text{products}$),

and to higher molecularity reactions are in progress, as well as the approach to steady state. Our new approach to low-dimensional chemical kinetics might lead to a new understanding for heterogeneous reactions of technological and biological importance.

We want to thank Len Sander, Robert Parson, Laurel Harmon, and other group members for helpful discussions, and The University of Michigan for computer and supercomputer funding.

^aSupported by the Department of the Army, Grant No. ARO DAAG 29-83-K-0131.

¹U. Even, K. Rademann, J. Jortner, N. Manor, and R. Reisfeld, *Phys. Rev. Lett.* **42**, 2164 (1984).

²T. A. Witten and L. M. Sander, *Phys. Rev. Lett.* **46**, 1400 (1981).

³R. Kopelman, in *Radiationless Processes in Molecules and Condensed Phases*, edited by F. K. Fong (Springer, Berlin, 1976), Vol. 15, p. 297.

⁴P. G. de Gennes, *Recherche* **7**, 919 (1976).

⁵P. Argyrakis and R. Kopelman, *Phys. Rev. B* **22**, 1830 (1980).

⁶S. Alexander and R. Orbach, *J. Phys. Lett. Paris* **43**, L625 (1982).

⁷Y. Gefen, A. Aharony, and S. Alexander, *Phys. Rev. Lett.* **50**, 77 (1983).

⁸A. Aharony and D. Stauffer, *Phys. Rev. Lett.* **52**, 2368 (1984).

⁹P. Argyrakis and R. Kopelman, *J. Chem. Phys.* **81**, 1015 (1984).

¹⁰R. Kopelman and P. Argyrakis, *J. Chem. Phys.* **72**, 3053 (1980).

¹¹P. G. de Gennes, *J. Chem. Phys.* **76**, 3316 (1982).

¹²P. W. Klymko and R. Kopelman, *J. Lumin.* **24/25**, 457 (1981).

¹³P. W. Klymko and R. Kopelman, *J. Phys. Chem.* **86**, 3686 (1982).

¹⁴P. W. Klymko and R. Kopelman, *J. Phys. Chem.* **87**, 4565 (1983).

¹⁵R. Kopelman, J. Hoshen, J. S. Newhouse, and P. Argyrakis, *J. Stat. Phys.* **30**, 335 (1983).

¹⁶A. Blumen, J. Klafter, and G. Zumofen, *Phys. Rev. B* **27**, 3429 (1983).

¹⁷P. G. de Gennes, *Chem. R. Acad. Sci. Paris* **296**, 881 (1983).

¹⁸P. Evesque, *J. Phys.* **44**, 1217 (1983).

¹⁹P. Evesque and J. Duran, *J. Chem. Phys.* **80**, 3016 (1984).

²⁰K. Kang and S. Redner, *Phys. Rev. Lett.* **52**, 955 (1984).

²¹R. Kopelman, P. W. Klymko, J. S. Newhouse, and L. W. Anacker, *Phys. Rev. B* **29**, 3747 (1984).

²²P. Meakin and H. E. Stanley, *J. Phys. A* **17**, L173 (1984).

²³P. Argyrakis and R. Kopelman, *Phys. Rev. B* **29**, 511 (1984).

²⁴R. Rammal and G. Toulouse, *J. Phys. Lett. Paris* **44**, L13 (1983).

²⁵L. W. Anacker, R. Kopelman, and J. S. Newhouse, *J. Stat. Phys.* **36**, 591 (1984).

²⁶J. S. Newhouse, P. Argyrakis, and R. Kopelman, *Chem. Phys. Lett.* **107**, 48 (1984).

²⁷P. Argyrakis, L. W. Anacker, and R. Kopelman, *J. Stat. Phys.* **36**, 579 (1984).

²⁸L. W. Anacker, P. W. Klymko, and R. Kopelman, *J. Lumin.* (in press).

²⁹Preliminary steady-state simulation results on percolating clusters give $X = 2.51$, J. S. Newhouse and R. Kopelman (unpublished).

³⁰R. M. Noyes, *Prog. React. Kinet.* **1**, 128 (1961).

³¹D. C. Torney and H. M. McConnell, *J. Phys. Chem.* **87**, 1441 (1983).

³²D. C. Torney, *J. Chem. Phys.* **79**, 3606 (1983).

³³D. F. Calef and J. M. Deutsch, *Annu. Rev. Phys. Chem.* **34**, 493 (1983).