PHYSICAL REVIEW
LETTERS

VOLUME 58 26 JANUARY 1987 NUMBER 4

Steady-State Chemical Kinetics on Fractals: Segregation of Reactants

L. W. Anacker and R. Kopelman
Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109
(Received 18 June 1986)

Supercomputer simulations of the elementary $A+B\rightarrow 0$, diffusion-limited reaction were performed under *steady-source* conditions, on a cubic and a fractal lattice. While both reaction orders have the classical value ($X=2$), a dramatic segregation ("morphogenesis") appears for the Sierpiński-gasket "lattice." This is relevant to chemical reactions on heterogeneous catalysts, to annealing of radiation damage and electron-hole recombination in inhomogeneous media, to charge polarization in clouds, and to possible matter-antimatter distributions in a steady-state universe.

PACS numbers: 05.40.+j, 82.20.Wk

Standard chemical kinetic relationships no longer apply for the diffusion-limited transient reactions,[1-15]

$$A+A\rightarrow \text{products}$$

or

$$A+B\rightarrow 0$$

in low-dimensional media and on fractal surfaces,[16] where $\rho\equiv\rho_A(t)=\rho_B(t)$ is a monotonically decreasing function of time t. The reaction kinetics in these systems are well described by

$$-d\rho/dt=k_0\rho^X,\quad t\rightarrow\infty, \tag{1}$$

where

$$X=\begin{cases}1+f^{-1} & (A+A \text{ reaction}),\\ 1+2f^{-1} & (A+B \text{ reaction}),\end{cases}$$

with spectral dimension[17,18] $d_s=2f$ and $0\leq f\leq 1$. For the steady-source reaction $A+A\rightarrow A$, the system is well described[19-21] by the following rate law:

$$-d\rho/dt=k_0\rho^X-R, \tag{2}$$

where R is the constant rate of walker addition, and $X=1+f^{-1}$. After the $A+A$ reaction reaches a steady state, this same power-law relation holds[19-21]

$$R=k_0\rho_{ss}^X, \tag{3}$$

where ρ_{ss} is the steady-state density achieved under steady-source conditions. For the $A+B\rightarrow 0$ reaction we report some unexpected results for the value of X [Eq. (3)]; furthermore, there is a dramatic segregation of reactants at the steady state.

The transient $A+B$ reaction has been of recent interest due to astrophysical considerations involving possible matter-antimatter distributions based on the "big-bang" theory of the universe.[22] The transient $A+B$ reaction is fundamentally different from the $A+A$ reaction since the Toussaint-Wilczek effect,[9-11,22] i.e., the $f/2=d_s/4$ behavior, is dependent on the formation of clusters of A and clusters of B. These clusters are formed only at very long times and consequently very low densities.[9-11] The Toussaint-Wilzcek effect may represent so delicate a balance that even very low rates of walker addition might destroy it. It is not clear whether the effect of clustering will survive under steady-source conditions which act to stir the system; it is not even clear whether steady-source conditions will necessarily establish a steady state. This is of much interest to continuous creation models of the universe, charge polarization in clouds, biochemical "morphogenesis,"[23] heterogeneous chemical catalysis, amorphous semiconductors, and photoelectric cells.

Simulations of the $A+B$ reaction under steady-source conditions were performed on the linear lattice ($f=\frac{1}{2}$, the planar Sierpiński gasket ($f=0.68$), and the simple

TABLE I. Steady-state densities.

Sierpiński gasket		Simple cubic lattice	
RM	ρ_{ss}	RM	ρ_{ss}
4	0.053	1	0.0067
2	0.039	$\frac{1}{4}$	0.0034
1	0.027	$\frac{1}{25}$	0.0013
		$\frac{1}{50}$	0.00094
		$\frac{1}{100}$	0.00067

cubic lattice ($f=1$). Random walkers of type A and B were added at a constant rate, R, and had an equal probability of landing on any unoccupied site. Each walker moved with probability z^{-1} to any of its z nearest-neighbor sites. Only one walker was allowed to occupy each site, and the $A+B$ reaction occurred when an A walker tried to move to a site occupied by a B walker or vice versa. Each system was followed for 10^6 steps with 10 to 20 realizations for each value of R. The rates of addition are reported (see Table I) in units of RM =number of A (=number of B) walkers added per number of time steps, i.e., $RM=\frac{1}{25}$ implies one A and one B walker were added after every 25 time steps on an M-site structure. The planar Sierpiński gasket ($M=9843$ sites) used values of $RM=1$, 2, and 4; the linear lattice ($M=25000$ sites) used values of $RM=\frac{1}{4000}$, $\frac{1}{1000}$, $\frac{1}{400}$, $\frac{1}{100}$, $\frac{1}{25}$, and 1, and the simple cubic lattice ($M=25^3$ sites) used values of $RM=\frac{1}{100}$, $\frac{1}{50}$, $\frac{1}{25}$, $\frac{1}{4}$, and 1. Periodic boundary conditions were used for the Euclidean lattices; the Sierpiński gasket was implemented with reflective boundaries at each of the three vertices of the largest triangle. A nonlinear regression, with R as the independent variable and $\langle\rho_{ss}\rangle$ as the dependent variable, was used to obtain X via Eq. (3), including the fixed point $R=0$, $\langle\rho_{ss}\rangle=0$. The simulations were performed on the Control Data Corporation Cyber-205 computer at Colorado State University.

The linear lattice simulations show a *segregation* into A clusters and B clusters. However, even 10^6 steps were not enough to establish a steady state (defined by densities constant in time). The average density kept increasing monotonically with time. The Sierpiński gasket and the cubic lattice did show the establishment of a steady state. These steady-state densities are reported in Table I, and snapshots of A and B walker distributions on the millionth step are presented in Figs. 1 and 2 for independent realizations on the cubic lattice and the Sierpiński gasket, respectively. The most striking effect is that segregation occurs under steady-source conditions for the fractal Sierpiński gasket ($\langle\rho_{ss}\rangle=0.05$) while no segregation is evident for the simple cubic lattice ($\langle\rho_{ss}\rangle=0.07$).

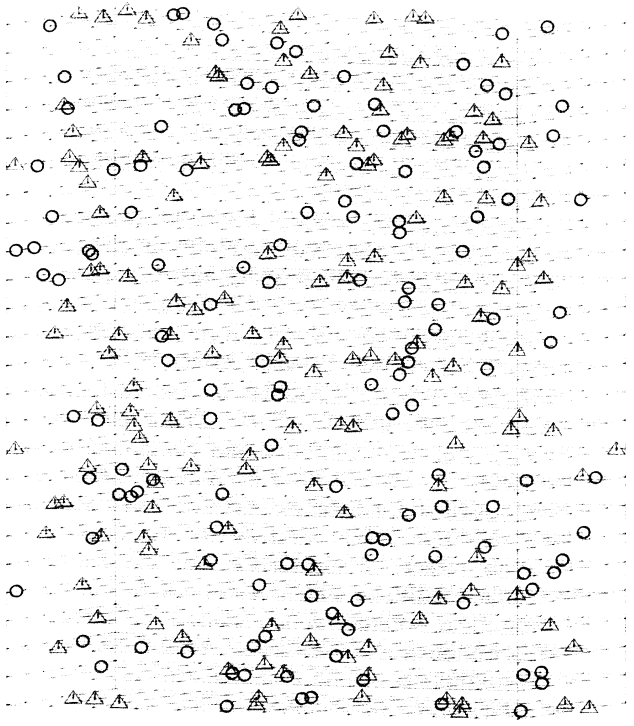

FIG. 1. A snapshot of the *steady-state* distribution, $\langle\rho_{ss}\rangle=0.07$, of molecules A (spheres) and B (triangles) in a simple cubic lattice. Note the random distribution. It takes about 10^4 time steps to establish the steady state. Shown is $\frac{1}{8}$ of the simulated lattice (of a single realization).

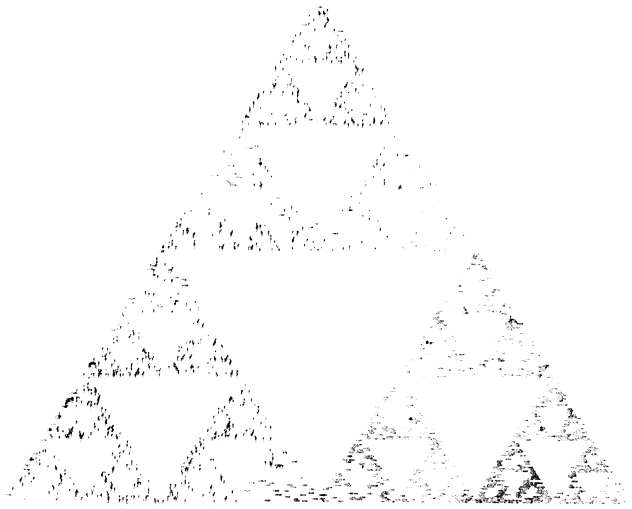

FIG. 2. A snapshot of the *steady-state* distribution of molecules A (vertical bars) and B (horizontal bars) on a fractal structure (a "Sierpiński gasket"). Note the segregated distribution. It takes about a million time steps to establish the steady state. During each time step every molecule moves at random. Altogether about 8×10^6 molecules landed at random, moved at random, and participated in this "annihilation" game. Note that the number of A and B molecules is kept strictly equal, at all times (the red-dominated area is thus about twice as dense as the blue one in this realization, $\langle\rho_{ss}\rangle=0.05$).

We note that Fig. 1 represents only $\frac{1}{8}$ of the total cubic lattice simulated. We also note that Fig. 2 represents an extremely asymmetric realization. The "blue" molecules dominate $\frac{2}{3}$ of the area while the "red" molecules are limited to nearly $\frac{1}{3}$ of the area (in spite of the fact that there are *equal* numbers of red and blue molecules, because of the strict A to B ratio requirements of the algorithm). While the symmetry aspects vary from realization to realization, they all exhibit dramatic segregation, for all densities and all R values.

On the cubic lattice, the Toussaint-Wilczek effect is lost, once the steady source of walkers is included. In contrast with their transient $A+B$ results, which translate to $X=3$ in Eq. (2), the steady-state $A+B$ results give $X=2.00\pm0.02$, with use of Eq. (3), for densities as low as 0.1%. While the Toussaint-Wilczek transient system results in segregation of the reactants, A and B, no such segregation is found for the steady state (see Fig. 1). These differences between the transient and steady-state results are attributed to a net effect of stirring caused by the steady addition of randomly distributed walkers. Transport on the simple cubic lattice is so efficient that even a very slow rate of walker addition is sufficient to cause a breakdown of the $X=1+2f^{-1}$ rule, Eq. (1).

On the other hand, the Sierpiński gasket under steady-source conditions shows dramatic segregation of A and B clusters. As pointed out for the cubic lattice, this steady-state segregation ("morphogenesis"[23] cannot be simply attributed to the Toussaint-Wilczek effect. Under *steady-source* conditions the Sierpiński gasket ($f=0.68$) yields $X=2.0\pm0.2$; neither the $X=1+2f^{-1}=3.9$ rule nor the $X=1+f^{-1}=2.5$ rule is followed. Steady-state densities are reported in Table I; however, local densities may vary considerably. High-density behavior for the $A+B$ reaction may be expected to yield $X=2$ in analogy with the high-density results for the $A+A$ steady-state problem,[19] but the cause for the observed segregation is not obvious. We note that very low-density simulations are orders of magnitude more difficult.

In conclusion, the $A+B\rightarrow 0$ reaction under steady-source conditions is totally different from the transient $A+B$ reaction. For the linear and Sierpiński lattices, the results for the $A+B$ reaction under steady-source conditions show large density fluctuations, and an increasing segregation during the approach to the steady state. For the linear lattice, a steady state is *not* obtained, even after 10^6 steps.[24] A steady state is observed for the (finite) fractal Sierpiński gasket and the simple cubic lattice where the kinetics are well described by Eq. (3). A value of $X=2$ holds for the simple cubic lattice and the Sierpiński gasket. In contrast with the cubic lattice, on the Sierpiński gasket we do find the surprising result of A and B segregation at steady state. This is reached only after the local segregation fluctuations have been converted to large-scale segregation ("morphogenesis").

We would especially like to thank L. Li and Dr. L. Harmon for the computer grahics presented here. This work was supported by National Science Foundation Grant No. DMR-83-03919 and U. S. Army Grant No. 29-83-K-0131.

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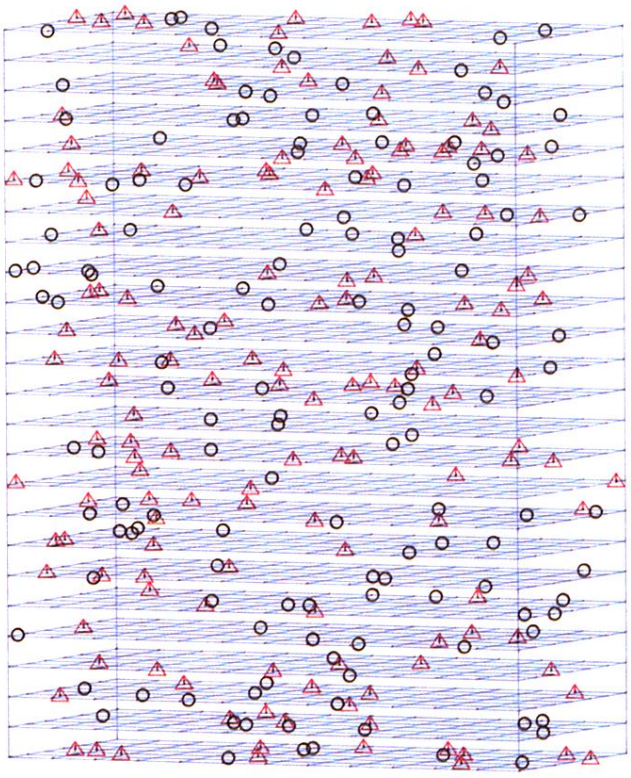
[24]For significantly shorter linear lattices, at high densities, a steady state, with segregation, has been documented by E. Clement, J. Hoshen, and R. Kopelman, unpublished.



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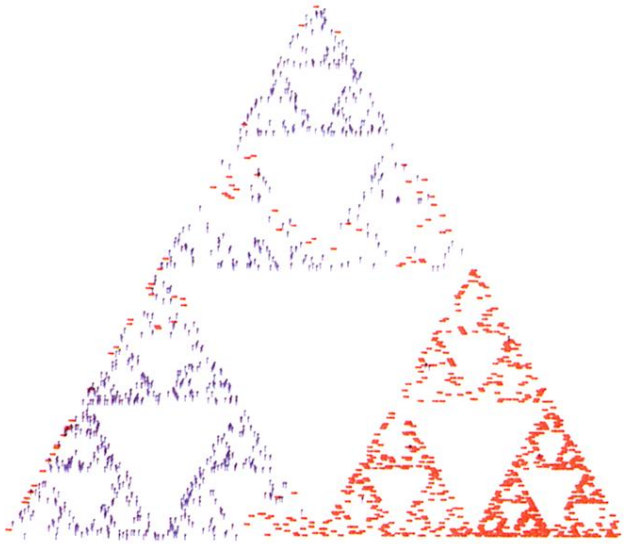

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