PHYSICAL REVIEW A VOLUME 39, NUMBER 12 JUNE 15, 1989

Steady-state diffusion-controlled $A + A \rightarrow 0$ reaction in Euclidean and fractal dimensions: Rate laws and particle self-ordering

Eric Clément
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109
and Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

Leonard M. Sander
Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

Raoul Kopelman
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

(Received 20 December 1988)

For diffusion-limited reactions of the type $A + A \rightarrow 0$, we present a theory for the pair correlation function and the macroscopic reaction law for the Euclidean dimensions $d=1$, 2, 3 and for self-similar fractal structures with spectral dimension such that $1 \le d_s \le 2$. In any dimension we define a length Λ, which is the typical size of the depletion zone around each particle. Λ is expressed as a function of a fundamental size $\xi = \sqrt{\rho D/R}$, where ρ is the steady-state density, R the external source rate, and D the microscopic diffusion constant. For $d_s \le 2$, we obtain the "fractal" reaction order $X = 1 + 2/d_s$ and a mesoscopic, density-dependent depletion zone around each particle. We give an interpretation of the particle self-ordering and anomalous rate laws in terms of the random-walk topological properties.

I. INTRODUCTION

The study of the diffusion-limited annihilation of the type $A + A \rightarrow 0$ is relevant in many areas of physics and chemistry such as studies of exciton annihilation processes in molecular crystals, porous glasses or polymers, and heterogeneous catalysis reaction kinetics.[1] In the case where the dimension of the substrate is not a three-dimensional Euclidean space, numerous experimental, theoretical, and numerical simulation studies[1–8] have been carried out. It is currently understood that in restricted geometries the reaction process may lead to nontrivial spatial correlations of the reactants.[5–8] In the case where the system starts from an initial random distribution of particles and decays, the decay rate is found to be anomalous for dimensions $d \le 2$ (fractal sets included).[1–3] Also, for a steady rate of arrival of particles, in $d=1$, it was shown that the effective order of the reaction is not the classical answer $X=2$, but $X=3$.[1,3,4] This result is due to spatial correlations of the reactants at steady state.[5–8] Moreover, from a scaling conjecture,[1,3] it was demonstrated that $X = 1 + d_s/2$ for the spectral dimension $d_s < 2$ and $X=2$ for $d_s > 2$.

In this paper we give a unified treatment for $d=1,2,3$ and fractal substrates for steady-state conditions. The theory we propose is based on a multiparticle correlation density analysis. We show that, in the low-density limit, the classical multiparticle hierarchy of equations can be truncated in a consistent way at the level of the two-particle density function. The set of two equations resulting from this procedure can be solved in the low-density limit and it captures the essential physical features of the problem. We relate the magnitude of the self-ordering of reactants to the properties of the random walk in the different dimensions considered.

II. EUCLIDEAN SPACES

We consider a d-dimensional Euclidean space on which identical particles "A" diffuse freely. Two-body annihilation occurs whenever two particles come in contact at a distance less or equal to a, the size of a particle. we assume that a source produces a fixed *external* rate R of particles per unit time and volume. We examine two types of sources: hard-core exclusion or vertical annihilation. A particle landing on the top of another one is either discarded (in the hard-core exclusion case), or a pair is annihilated for the vertical-annihilation case. In any case, the *effective* rate of arrival is less than R and denoted by Q. We also consider the possibility of an internal first-order decay in conjunction with a nonvertical annihilation source. The internal decay, of the type $A \rightarrow 0$, is controlled by a fixed rate λ. We explicitly consider these three cases for their practical importance and also because for reactions of the type $A + B \rightarrow 0$, the exact definition of the source term is an essential feature controlling the kinetics.[9]

In order to derive the equations of motion for the one- and two-particle density functions, we discretize the medium onto a d-dimensional square lattice at the scale of the particle size a. Then we introduce ρ_j, the local particle density, which is unity if a particle A is present at the site j and zero otherwise. The spatial and statistical average of this quantity is the one-particle density $\rho(t)$. The two-particle density f_k is the average over space and realizations of the quantity $\rho_j \rho_{j+k}$ (the indices

j and k are d-dimensional lattice indices). The continuum limit of f_k is denoted $f(\mathbf{r},t)$.

The equation of motion for the overall density $\rho(t)$ is

$$\dot{\rho}(t)=Q(t)-J_{AA}(t)\ ,$$

where $Q(t)$ is the effective source term, which may include the internal decay contribution, and $J_{AA}(t)$ is the reaction term. For the nonvertical annihilation process, a particle attempting to land on an already occupied site is discarded. The contribution to the derivative of ρ_i is $R(1-\rho_i)$. In the other case (vertical annihilation), a particle landing on top of another particle reacts and annihilates with this other particle. This adds $-R\rho_i$ to the previous contribution. In the first-order-decay case, the extra contribution to the nonvertical annihilation source term is $-\lambda\rho_i$. After spatial and statistical averaging of these contributions, and after going to the continuum limit, we obtain

$$Q(t)=R[1-v\rho(t)]$$

with $v=a^d$ for the nonvertical-annihilation case, $v=2a^d$ in the vertical-annihilation case, and $v=a^d+\lambda/R$ in the internal decay case. In any case, v is an effective excluded volume that modifies the external rate of arrival. Since we describe a diffusion-limited process we know that $J_{AA}(t)$ is given by the Smoluchowski boundary condition[9-11]

$$J_{AA}(t)=2D\int_{\Sigma}d\mathbf{S}\cdot\nabla f(\mathbf{r},t)\ .$$

After assuming a statistically isotropic distribution near the particles, we can write the first hierarchic equation:

$$\dot{\rho}(t)=Q(t)-2D\Omega_d a^{d-1}\left.\frac{\partial f(\mathbf{r},t)}{\partial r}\right|_{r=a} \tag{1}$$

with Ω_d the solid angle in dimension d.

The second hierarchic equation is the equation of motion for the two-particle density correlation $f(\mathbf{r},t)$. The condition of instantaneous reaction at a close contact ensures a natural truncation at the three-particle level and therefore

$$\dot{f}(\mathbf{r},t)=F_D+S+F_2+F_3\ , \tag{2}$$

where F_D is a diffusion term, S is a source term, F_2 is a two-particle contribution, and F_3 is a three-particle contribution. The source term is obtained considering all the elementary contributions to the variation of $\rho_j\rho_{j+k}$ per unit of time. In a nonvertical-annihilation case, one has $R\rho_j(1-\rho_{j+k})+R\rho_{j+k}(1-\rho_j)$. In the vertical-annihilation case, one adds to the previous term the vertical reaction contribution $-2R\rho_j\rho_{j+k}$. For the internal decay, the extra contribution is $2\lambda\rho_j\rho_{j+k}$. After spatial and statistical averaging and in the continuum limit, we obtain

$$S=2R\rho(t)-2Rvf(\mathbf{r},t)\ .$$

In the lattice model, the two-particle annihilation contribution F_2 is nonzero if $j+k$ is a nearest neighbor of j. We obtain $-2(\Gamma/Z_d)\rho_j\rho_{j+k}$, where Γ is the intrinsic jump rate and $Z_d=2d$ is the number of nearest neighbors. After averaging and in the continuum limit, we have

$$F_2=-2D\left.\frac{\partial f(\mathbf{r},t)}{\partial r}\right|_{r=a}\delta_{r-a}\ ,$$

where $\Gamma a^2/Z_d$ is replaced by D, the diffusion constant, and the kronecker symbol, limiting the extent of the contribution to the nearest neighbors, is replaced by $a\delta_{r-a}$. We also used the boundary condition $f(a,t)=0$ and expanded $f(\mathbf{r},t)$ up to the first order in a.

The F_3 term of Eq. (2) is a three-particle contribution. It can be visualized as resulting from two particles, at a distance $|\mathbf{r}|>a$ of a third one, reacting with each other. In a lattice formulation, this is the average of a term

$$(\Gamma/Z_d)(\rho_j\rho_{j+k}\rho_{j+k+k'}+\rho_j\rho_{j+j'}\rho_{j+k})\ ,$$

where $j+j'$ and $j+k+k'$ are nearest neighbors of j and $j+k$, respectively. We approximate this term by a function linear in $f(\mathbf{r},t)$ with an unknown coefficient $-2\alpha(t)$:

$$F_3=-2\alpha(t)f(\mathbf{r},t)\ .$$

This is a truncation scheme where only two particles are correlated and a third one is considered to exert an average influence. An identical approach was used by Waite[12] in order to evaluate short time corrections to the classical Smoluchowski rate constant in $d=3$. We systematically ignore the contributions where three particles are confined in the same microscopic volume. Thus, we expect this approximation to be valid in the low-density limit. Now Eq. (2) becomes

$$\dot{f}(\mathbf{r},t)=2D\nabla^2 f(\mathbf{r},t)-2(\alpha+vR)f(\mathbf{r},t)$$
$$-2D\left.\frac{\partial f(\mathbf{r},t)}{\partial r}\right|_{r=a}+2R\rho(t)\ . \tag{3}$$

The unknown parameter α is determined from the identity $(1/V)\int d\mathbf{r}\,f(\mathbf{r},t)=\rho(t)^2$, where V is the total volume. After integration over V of Eq. (3), we obtain

$$\dot{\rho}(t)=\frac{1}{V}D\left.\frac{\partial f(\mathbf{r},t)}{\partial r}\right|_{r=a}-(\alpha+vR)\rho(t)+R\ . \tag{4}$$

Then we compare (4) with (1), and in the thermodynamic limit ($V\rightarrow\infty$) we have

$$\alpha=\frac{R[1-v\rho(t)]-\rho(t)}{\rho(t)}\ ,$$

Inserting this value of α into expression (3), we obtain the equation of motion for $f(\mathbf{r},t)$:

$$\dot{f}(\mathbf{r},t)=2D\nabla^2 f(\mathbf{r},t)-\frac{2R[1-\rho(t)]}{\rho(t)}f(\mathbf{r},t)$$
$$-2D\left.\frac{\partial f(\mathbf{r},t)}{\partial r}\right|_{r=a}\delta_{r-a}+2R\rho(t)\ . \tag{5}$$

At steady state, Eq. (5) yields a differential equation describing the distribution of particles. For $r\geq a$

$$\nabla^2 f(\mathbf{r}) - \frac{R}{\rho D} f(\mathbf{r}) - \frac{Q}{2D}\frac{\delta_{r-a}}{\Omega_d a^{d-1}} + \frac{R\rho}{D} = 0 \ . \tag{6}$$

This is the central equation that we solve in various dimensions, with the condition for $r \le a$:

$$f(\mathbf{r}) = f(a) = 0 \ . \tag{7}$$

Also we must satisfy the Smoluchowski boundary condition at steady state:

$$Q = 2D\Omega_d a^{d-1} \left. \frac{\partial f(\mathbf{r})}{\partial r} \right|_{r=a} \ . \tag{8}$$

Inspection of Eq. (6) shows that a "natural" or "characteristic" length ξ arises and has a value

$$\xi = \sqrt{\rho D / R} \ . \tag{9}$$

Furthermore, dimensional analysis shows that we can replace $\partial f(\mathbf{r})/\partial r|_{r=a}$ by ρ^2/Λ, where Λ is an effective correlation length for the A-A pair distribution which characterizes the influence of the particle distribution on the reaction kinetics. It can also be interpreted as the characteristic size of a depletion zone around each particle. In the following, we will seek to express Λ as a function of the length ξ. Moreover, it is important to note that the particular form of the source term and the consideration of an internal decay mechanism enter Eq. (6) only indirectly in the effective rate constant Q. Therefore, these details do not influence the bimolecular reaction kinetics. This result contradicts that of Suna,[13] derived for the reaction kinetics of excitons where the decay mechanism is found to control the bimolecular reaction rate.

From a Fourier transformation, the solution of Eq. (6) is

$$f(\mathbf{r}) = \rho^2 - \frac{Q}{2D\Omega_d a^{d-1}} \int d\mathbf{q} \frac{\Phi_d(qa)}{q^2 + \xi^2} e^{-i\mathbf{q}\cdot\mathbf{r}} \ ,$$

where $\Phi_d(qa)$ is the Fourier transform of δ_{r-a}.

For $d=1$, we have $\Omega_1 = 2$, $\Phi_1(qa) = 2\cos qa$, and we obtain for $r \ge a$

$$f(\mathbf{r}) = \rho^2 - \frac{Q\xi}{4D} e^{-(r-a)/\xi} \frac{1 + e^{2a/\xi}}{2} \ .$$

Condition (8) imposes, for the theory to be consistent, that $a/\xi \ll 1$, and in this limiting case, considering the first condition (7), we obtain

$$f(r) = \rho^2 (1 - e^{-(r-a)/\xi}) \ .$$

The reaction law is $Q = (4D/\xi)\rho^2$, which implies that

$$\Lambda = \xi \ . \tag{10}$$

The effective reaction law is

$$Q = (1 - v\rho) = \frac{16D}{1 - v\rho} \rho^3 \ . \tag{11}$$

We have a nonclassical result and, in the low-density limit, an effective exponent of the density $X=3$. The exponent of 3 was also obtained exactly by Racz[4] and it agrees with computer simulations.[3] If we compare the prefactor 16 we found to the exact number 20.64, obtained in the exact calculation, we have a numerical agreement of approximately 25%. The anomalous effective exponent is also a result obtained by Peacock-Lopez and Keizer,[14] for the reaction $A + A \to A + P$, using an approximate theory based on fluctuation-dissipation theorem. It is also noted that this length ξ is proportional to the maximum of the nearest-neighbor distance distribution.[7]

For $d=2$, we have $\Omega_2 = 2\pi a$ and $\Phi_2(aq) = 2\pi a J_0(aq)$, where $J_0(aq)$ is a Bessel function of the first kind.[15] Thus, $f(\mathbf{r})$ (Ref. 16) is

$$f(\mathbf{r}) = \rho^2 - \frac{Q}{4\pi D} I_0(a/\xi) K_0(r/\xi) \ ,$$

where $I_0(z)$ and $K_0(z)$ are modified Bessel functions.[15] Condition (8) requires that $a/\xi \ll 1$ and, in this limit, we have for $r \ge a$

$$f(\mathbf{r}) = \rho^2 \left[1 - \frac{K_0(r/\xi)}{K_0(a/\xi)} \right]$$

and the macroscopic law

$$Q = R(1 - v\rho) = \frac{4\pi D}{C_0 + \ln\xi/a} \rho^2 = \frac{4\pi D}{C_0 + \frac{1}{2}\ln\frac{\rho D}{a^2 R}} \rho^2 \tag{12}$$

with $C \cong 0.577$ the Euler constant, $C_0 = \ln 2 - C \cong 0.116$, and

$$\Lambda = C_0 - \ln\xi/a \ . \tag{13}$$

This macroscopic law is totally nonclassical and cannot be cast in the form of an effective power law.

For $d=3$, we have $\Omega_3 = 4\pi a^2$ and $\Phi_3(aq) = -4\pi a \sin qa/q$, and $f(\mathbf{r})$ is

$$f(\mathbf{r}) = \rho^2 - \frac{Q}{8\pi D} \frac{e^{-r/\xi}}{r} \frac{\sinh(a/\xi)}{a/\xi} \ .$$

To satisfy the boundary conditions (8), we obtain for $a/\xi \ll 1$ the expression

$$f(\mathbf{r}) = \rho^2 \left[1 - \frac{a e^{-(r-a)/\xi}}{r} \right]$$

and the macroscopic reaction law

$$Q = R(1 - \beta\rho) = 8\pi D a \rho^2 \tag{14}$$

which is the classical Smoluchowski result[10–12] and the depletion zone is of the order of $\Lambda = a$.

III. EXTENSION TO FRACTAL SETS

For a self-similar fractal structure characterized by the geometrical fractal dimension d_f and the spectral dimension d_s,[17–20] we propose a theory generalizing the previous results. For a random walk on a self-similar fractal structure, the distribution of particles in the fractal is highly discontinuous (and this at every length scale), but the envelope $c(\mathbf{r},t)$ of this distribution is smooth and is a solution of the generalized Fick equation[21]:

$$c(\mathbf{r},t)=K\frac{1}{r^{d-1}}\frac{\partial}{\partial r}r^{d-1-\theta}\frac{\partial}{\partial r}c(\mathbf{r},t)\ .$$

θ is the anomalous diffusion exponent defined by the relation $\theta=2(d_f/d_s-1)$. The constant K depends on the geometry of each fractal set and is related to the scale-dependent diffusion constant $D(r)$ through the relationship $D(r)=Kr^{-\theta}$. We note that this result is obtained after averaging on a collection of identical fractal sets with different orientations in order to render the problem essentially isotropic. Also, it is important to realize that an implicit cut off was performed in the fractal at the size of the particles and this procedure defines a volume for the fractal embedded in the Euclidean space. Therefore, all the densities we define are normalized to this "fractal volume." For example, $c(\mathbf{r},t)dv_f(\mathbf{r})$ represents the probability that a particle is on the fractal in a small volume $d\mathbf{r}$ around $\mathbf{r}$, where $dv_f(\mathbf{r})$ is the volume of the fractal in $d\mathbf{r}$. We transpose Eq. (6) into the fractal domain using the generalized Fick equation to express the diffusion operator acting on the envelope of the two-particle density function [denoted $\tilde{f}(\mathbf{r},t)$]. We note that a similar method using the generalized Fick equation was successfully used in the case of a decay of particles from a random initial distribution, in order to explain the anomalous behavior of the decay exponent.[22] Therefore, at steady state, we seek to solve the following equation for $r\geq a$:

$$K\frac{1}{r^{d_f-1}}\frac{\partial}{\partial r}r^{d_f-1-\theta}\frac{\partial}{\partial r}\tilde{f}(\mathbf{r})-\frac{R}{\rho}\tilde{f}(\mathbf{r})+R\rho =\frac{Q}{2_a\Sigma_{d_f}}\delta_{r-}\ , \qquad (15)$$

where the microscopic diffusion constant

$$D=D(a)=Ka^{-\theta}$$

and Σ_{d_f} is the reaction surface. For $r\leq a$, $f(r)=f(a)=0$, and the Smoluchowski boundary condition is

$$Q=Ka^{-\theta}\Sigma_{d_f}\left.\frac{\partial\tilde{f}(\mathbf{r},t)}{\partial r}\right|_{r=a}=Ka^{-\theta}\Sigma_{d_f}\frac{\rho^2}{\Lambda}\ .$$

We define $g(\mathbf{r})=\rho^2-f(\mathbf{r})$ and then, for $r>a$ and $g(a)=\rho^2$, we solve the differential equation

$$K\frac{1}{r^{d_f-1}}\frac{\partial}{\partial r}r^{d_f-1-\theta}\frac{\partial}{\partial r}g(\mathbf{r})-\frac{R}{\rho}g(\mathbf{r})=0\ . \qquad (16)$$

Equation (16) is transformed into

$$g''(z)+\frac{d-1-\theta}{z}g'(z)-\left[\frac{\xi}{a}\right]^{\theta}z^{\theta}g(z)=0 \qquad (17)$$

where $z=r/\xi$, $\xi=\sqrt{\rho D/R}$. Solutions of Eq. (17) are[15] $g(z)=z^{\beta\nu}Z_\nu(\gamma z^{\beta})$, where $Z_\nu(z)$ is a Bessel function and $d_s\leq 2$

$$\beta=1+\frac{\theta}{2}=\frac{d_f}{d_s}\ ,$$

$$\upsilon=1-\frac{d_f}{2+\theta}=1-\frac{d_s}{2}\ ,$$

$$\gamma=\pm i\frac{1}{1+\theta/2}\left[\frac{\xi}{a}\right]^{\theta/2}=\pm i\frac{d_s}{d_f}\left[\frac{\xi}{a}\right]^{d_f/d_s-1}\ .$$

The particular Bessel function that fits the boundary conditions is the modified Bessel function[15] $\mathbf{K}_\nu(z)$. We notice that this result extends to the particular cases $d_f=d_s=1$ and also $d_f=d_s=2$. Using the boundary condition $g(a)=\rho^2$, we finally obtain

$$\tilde{f}(\mathbf{r})=\rho^2\left[1-\left[\frac{r}{a}\right]^{\beta\nu}\frac{\mathbf{K}_\nu((a/\beta\xi)(r/a)^{\beta})}{\mathbf{K}_\nu(a/\beta\xi)}\right]\ .$$

Since $\mathbf{K}_\nu(z)\approx\sqrt{(\pi/2z)}e^{-z}$ when $z\rightarrow\infty$, the limit of $f(\mathbf{r})$ for $r\rightarrow\infty$ is ρ^2. To find the macroscopic law of reaction and the depletion length Λ, we calculate $\partial\tilde{f}(\mathbf{r})/\partial r|_{r=a}\equiv\frac{\rho^2}{\Lambda}$. We obtain

$$\Lambda=\xi\frac{\mathbf{K}_\nu\left[\frac{a}{\beta\xi}\right]}{\mathbf{K}_{1-\nu}\left[\frac{a}{\beta\xi}\right]}\ .$$

In the limit where $a/\xi\ll 1$

$$\Lambda=aC_\nu(2\beta)^{2\nu-1}\left[\frac{\xi}{a}\right]^{2\nu}$$

or, as a function of the fractal and spectral dimensions (for $1\leq d_s\leq 2$),

$$\Lambda=aC_{1-d_s/2}\left[\frac{d_s}{2d_f}\right]^{d_s-1}\left[\frac{\xi}{a}\right]^{2-d_s}\ . \qquad (18)$$

A priori, C_ν depends also on ξ and β. For large values of ξ/a such that $\xi/a>>e^{1/2-d_s}$, coefficient C_ν has the constant limiting expression

$$C_\nu=\frac{\Gamma(\nu)}{\Gamma(1-\nu)}=\frac{\Gamma(1-d_s/2)}{\Gamma(d_s/2)}\ .$$

For the intermediate values of ξ/a, or more precisely, for $1\ll\xi/a\ll e^{1/2-d_s}$, C_ν has the limiting expression

$$C_{1-d_s/2}=\frac{1}{2}\left[C_0+\ln\frac{d_f\xi}{d_sa}+O(\nu)\right]\ .$$

Therefore, in the limit where $\nu=0$ or $d_s=2$, we recover the result for the Euclidean dimension $d=2$.

From this result we obtain the reaction law

$$Q=\frac{2D\Sigma_{d_f}\rho^2}{aC_{1-d_s/2}\left[\frac{d_s}{2d_f}\right]^{d_s-1}\left[\frac{\xi}{a}\right]^{2-d_s}}\ . \qquad (19)$$

It is important to notice that, as in Euclidean dimensions, the condition $a/\xi\ll 1$ is essential for the differential equation (15) to satisfy the δ-function requirement at $r=a$. In the low-density limit, which is actually the same as the limit $a/\xi \rightarrow 0$, one obtains an effective reaction law $R \approx \rho^X$, with the effective order of reaction

$$X = 1 + d_s/2 \quad \text{and} \quad d_s < 2 \; . \tag{20}$$

This relation was found previously by Anacker, Parson, and Kopelman[3] as the result of a conjecture on the *time dependence* of the effective rate constant. This approach was based on considerations involving the behavior of a single random walker. The structure of this exponent was verified by simulations on various self-similar fractal structures such as Sierpinski gaskets, Sierpinski carpets, and percolation clusters,[1,3] and was also found experimentally.[3] We note that ν is the same as the heterogeneity exponent[3] h.

IV. RANDOM WALKS AND SELF-ORDERING

The results of the previous sections can be put in an interesting way, if we link the self-ordering of the system (multiparticle effect) to the fundamental properties of a single random walker. Note first that $\tau \approx \rho/R$, is the typical lifetime of the particles because, for any volume V, large enough to contain several correlation lengths Λ, the number of particles arriving during a time τ ($\approx VR\tau$), is equal to the number of particles originally present in the system ($\approx \rho V$). Since we are at steady state, this number must remain constant. Thus, τ is the typical time of renewal of the population (or the typical individual lifetime). From Eq. (9), $\tau \sim \xi^2$. We call V_N the total volume that a particle sweeps out during a random walk of N steps. In a continuum description we have $N \equiv \Gamma\tau$ and $V_\tau = \sigma a \Gamma \tau$, where σ is the cross section of a particle, a the typical jump distance, and Γ the typical rate of jump. Therefore, $V_N \approx N$ (or $V_\tau \sim \tau$). S_N is the number of distinct sites visited.[19,20] We recall that for $1 \le d_s < 2$, $S_N \approx N^{d_s/2}$; for $d=2$, $S_N \approx N/\ln N$, and for Euclidean lattices, for $d>2$, $S_N \approx N$. Thus, in any of the considered dimensions,

$$\frac{\Lambda}{a} \approx \frac{V_\tau}{S_\tau} \; . \tag{21}$$

The ratio S_τ/V_τ is called the efficiency of the random walk (analogous to the efficiency defined by S_N/V_N in Ref. 23) and when τ goes to infinity, it converges to the escape probability. Relation (21) links the magnitude of the multiparticle self-ordering to the compactness of the random walk.[11] The less efficient the random walker is in the exploration of its environment, the more the correlation grows in the steady state. It is worth noticing that, for the time-dependent or transient problem, Anacker *et al.*[3] conjectured that the effective rate constant scales like dS_t/dt, which is equivalent to having a time-dependent correlation length $\Lambda(t) \sim (dS_t/dt)^{-1}$.

V. CONCLUSIONS

From a simple theory based on a multiparticle hierarchy formalism, we gave here results consistent, in the low-density limit, with an exact theory[4] (in $d=1$), conjectures and computer simulations, and some experiments.[3,24] The theory is applied to Euclidean dimensions $d=1,2,3$ and is extended to self-similar fractal sets with spectral dimension d_s such that $1 \le d_s \le 2$. We derive the pair correlation function and the macroscopic law of reaction. We find a length Λ, appearing in the macroscopic reaction law, which is the typical size of the depletion zone around each particle. Λ is expressed [Eqs. (10), (13), and (18)] as a function of a fundamental characteristic size $\xi = \sqrt{\rho D/R}$, where ρ is the steady-state density, R the external source rate, and D the microscopic diffusion constant. Also, ξ is related to the characteristic lifetime of the particles: $\tau \approx \rho/R$. We find in the low-density limit (or $a/\xi \ll 1$) the correlation length Λ and the effective order of reaction X [Eqs. (11), (12), (19), and (20)].

For $1 < d_s < 2$ and for $\xi/a \gg e^{1/2-d_s}$

$$\Lambda = a \frac{\Gamma(1-d_s/2)}{\Gamma(d_s/2)} \left[\frac{d_s}{d_f}\right]^{d_s-1} \left[\frac{\xi}{a}\right]^{2-d_s} ,$$

$$X = 1 + d_s/2 ,$$

for $d = d_s = 2$:

$$\Lambda = a\,[C_0 + \ln(\xi/a)]$$

no effective order of reaction ,

for $d = d_s = 3$:

$$\Lambda = a, \quad X = 2 \; .$$

We can summarize these results as $\Lambda/a \approx V_\tau/S_\tau$, where $V_\tau \approx \tau$ is the total volume swept out by the random walker and S_τ is the volume effectively explored.

In contrast to the $A+B \rightarrow 0$ problem[9] and to other theoretical results,[13] we find at low density that hard-core exclusion in the source and reaction mechanisms such as vertical annihilation or first-order decay have no effect on the bimolecular reaction kinetics. Both these processes act as an effective exclusion volume modifying the effective rate of arrival of the particles.

ACKNOWLEDGMENTS

This research is supported by National Science Foundation Grants No. DMR-88-010120 (E.C. and R.K.) and No. DMR-88-15908 (L.S.).

---

[1] R. Kopelman, in *Transport and Relaxation in Random Materials*, edited by J. Klafter, R. J. Rubin, and M. F. Schlesinger (World Scientific, Singapore, 1986); Science **241**, 1620 (1988).

[2] K. Kang and S. Redner, Phys. Rev. Lett. **52**, 955 (1984); P. Evesque and J. Duran, J. Chem. Phys. **80**, 3016 (1984); P. W. Klymko and R. Kopelman, *ibid.* **87**, 4565 (1983).

[3] L. W. Anacker and R. Kopelman, J. Phys. Chem. **81**, 6402 (1984); L. W. Anacker, R. P. Parson, and R. Kopelman, *ibid.* **89**, 4758 (1985).

[4] Z. Racz, Phys. Rev. Lett. **55**, 1707 (1985).

[5] R. Kopelman and S. J. Parus, in *Fractal Aspect of Materials II,* edited by D. W. Schaefer, R. B. Laibowitz, B. B. Mandelbrot, and S. H. Liu (Materials Research Society, Pittsburgh, 1986).

[6] S. J. Parus and R. Kopelman, Phys. Rev. B **39**, 889 (1989); S. J. Parus, J. Prasad, and R. Kopelman, Chem. Phys. **128**, 209 (1988).

[7] L. Li, Ph.D. thesis, University of Michigan, 1989 (unpublished).

[8] C. Doering and D. Ben-Avraham, Phys. Rev. A **38**, 3035 (1988).

[9] E. Clément, L. Sander, and R. Kopelman, preceding two papers, Phys. Rev. A **40**, 6455 (1989); **40**, 6466 (1989).

[10] R. von Smoluchowski, Z. Phys. Chem. **29**, 129 (1917).

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

[12] T. R. Waite, Phys. Rev. **1**, 463 (1957).

[13] A. Suna, Phys. Rev. B **107**, 1716 (1970).

[14] E. Peacock-López and J. Keizer, J. Chem. Phys. **88**, 1997 (1988).

[15] I. S. Gradshteyn and I. M. Rhyzhik, in *Table of Integrals, Series and Products* edited by A. Jeffrey (Academic, New York, 1980).

[16] A. Erdélyi, *Tables of Integral Transforms II* (McGraw-Hill, New York, 1954).

[17] B. Mandelbrot, *The Fractal Geometry in Nature* (Freeman, San Francisco, 1982).

[18] S. Alexander and R. Orbach, J. Phys. Lett. **43**, 625 (1982).

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

[20] S. Havlin and D. Ben-Avraham, Adv. Phys. **34**, 693 (1987).

[21] B. O'Shaughnessy and I. Procaccia, Phys. Rev. A **32**, 3073 (1985).

[22] A. G. Vitukhnovsky, B. L. Pyttel, and I. M. Sokolov, Phys. Rev. A **126**, 89 (1987).

[23] J. Hoshen and R. Kopelman, J. Chem. Phys. **65**, 2817 (1976); R. Kopelman and P. Argyrakis, *ibid.* **72**, 3053 (1980).

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