

## The A + B → 0 Reaction under Short-Range Interactions

I. M. Sokolov,<sup>\*,†,‡</sup> P. Argyrakis,<sup>‡</sup> and A. Blumen<sup>†</sup>

*Theoretische Polymerphysik, Universität Freiburg, Rheinstrasse 12, D-79104 Freiburg i.Br., Germany; Department of Physics, University of Thessaloniki, 54006 Thessaloniki, Greece; and P. N. Lebedev Physical Institute of the Academy of Sciences of Russia, Leninsky prospect 53, Moscow 117924, Russia*

Received: November 8, 1993<sup>®</sup>

We consider here the A + B → 0 reaction between particles that diffuse, interact through short-range forces, and react on contact. In a plausible approximation the reaction can be described through a nonlinear diffusion equation, from which the scaling behavior of the respective A and B concentrations follows. We focus here on steady particle generation and obtain the exponents that govern the concentration's growth. Through explicit Monte Carlo simulations of the underlying stochastic process we obtain directly these exponents; furthermore we show that the assumption of particle segregation in clusters is correct, by computing the correlation length.

### Introduction

Although the investigation of diffusion-controlled chemical reactions dates back to Smoluchowski (1917),<sup>1</sup> some extremely important effects were understood only recently.<sup>2–14</sup> By now one can assert that, for example, the A + B → 0 reaction between uncharged particles is well-understood. Nonetheless there are very few results concerning reactions between particles which interact with each other through short-range forces. Although the case of particles interacting through screened electrostatic forces was considered already by Debye,<sup>15</sup> the multiparticle and fluctuation effects which determine the large-scale/long-time behavior of this reaction were seldom analyzed. A similar model for elastic forces (all particles attract each other) was investigated in ref 16.

In the present article we deal with the simplest model of an A + B → 0 reaction between interacting particles in one dimension under particle generation and try to elucidate the role of multiparticle effects. A simple analytical model for such a reaction was proposed in ref 17; here we review the theoretical approach and aim to assess the forecast of the analytical treatment through extensive Monte Carlo simulations of the reaction process. The situation considered corresponds to particles interacting through short-range forces. Here particles of the same kind repel each other, whereas particles of different kind attract each other; furthermore the reaction occurs on contact.

### Theoretical Model

**Main Equations.** In a continuous-medium approximation the kinetics of particles' concentrations  $n_A(\mathbf{x}, t)$  and  $n_B(\mathbf{x}, t)$  is governed by the equations

$$\partial n_A / \partial t = \nabla(D \nabla n_A - \alpha \nabla \mu_A \{n_A, n_B\} n_A) - R\{n_A, n_B\} + j_A(\mathbf{x}, t) \quad (1)$$

$$\partial n_B / \partial t = \nabla(D \nabla n_B - \alpha \nabla \mu_B \{n_A, n_B\} n_B) - R\{n_A, n_B\} + j_B(\mathbf{x}, t) \quad (2)$$

Here  $D$  is the diffusion coefficient (considered equal for both reacting species),  $\mu_A\{n_A, n_B\}$  and  $\mu_B\{n_A, n_B\}$  are the local chemical potentials for the particles of the two kinds,  $\alpha$  is the particles' mobility,  $R\{n_A, n_B\}$  is the reaction term, and  $j_A$  and  $j_B$  represent the generation rates (i.e., numbers of particles generated per unit

time per unit volume). The variables  $\mu_A$ ,  $\mu_B$ , and  $R$  are in general functionals of the particles' concentrations. We shall consider the stoichiometrical case, for which  $\langle j_A \rangle = \langle j_B \rangle = j$  holds.

Equations 1 and 2 represent the standard approximation and we start from them; we note, however, that the reaction terms may be quite complex (especially in low dimensions) and may even depend on correlation functions of higher order than  $n_A$  and  $n_B$  (see, e.g., ref 9). The approximate character of eqs 1 and 2 does not influence much the asymptotical short- and long-term regimes; therefore we can use eqs 1 and 2 when we focus on the scaling behavior of the concentrations and of the correlation functions.

To obtain the short- and the long-time behavior from eqs 1 and 2, we will use different approximations. We shall see that while the short-time regime is simple, the problem of the long-time behavior can be reduced to a nontrivial, nonlinear diffusion equation, related to expressions describing the growth of rough interfaces.

We start from the very simple short-time situation. Immediately after switching the particles' generation on, the concentrations are so low that the generated particles hardly interact and do not react. Therefore the number of particles in the system is simply equal to the whole number of particles generated, whose mean concentration is

$$n(t) = \langle n_A(t) \rangle = \langle n_B(t) \rangle = jt \quad (3)$$

This simple discussion is necessary in order to obtain later on an estimate for the crossover time to the other, fluctuation-dominated regime. Now we turn to this long-time regime, whose behavior is much less trivial.

For extremely fast reactions ( $R \rightarrow \infty$ ) in low-dimensional spaces and for long times there exist only nonpenetrating A and B clusters and the reaction takes place at the clusters' boundaries only. We set now  $q(\mathbf{x}, t) = n_A(\mathbf{x}, t) - n_B(\mathbf{x}, t)$  for the local concentration difference and put

$$n_A = q\theta(q) \quad n_B = -q\theta(-q) \quad (4)$$

In fact, for longer times eq 4 is well-obeyed even for finite reaction rates  $R$ , as shown in refs 13 and 14 for systems of noninteracting reacting particles. We will prove this in our case (interacting particles) through numerical calculations of the two-particle distribution functions. Note that eqs 4 imply  $n(t) = \langle n_A(\mathbf{x}, t) \rangle = \langle n_B(\mathbf{x}, t) \rangle = \langle |q(\mathbf{x}, t)| \rangle / 2$ .

Using eqs 1, 2, and 4 one can derive a closed differential equation that involves only  $q$ . In ref 17 it was shown for a special interaction model that the effective force acting on the particles is proportional

<sup>†</sup> Universität Freiburg.

<sup>‡</sup> University of Thessaloniki.

<sup>§</sup> P. N. Lebedev Physical Institute of the Academy of Sciences of Russia.

• Abstract published in *Advance ACS Abstracts*, June 15, 1994.

to the local gradient of  $q(\mathbf{x})$ . Our numerical simulations with different types of short-range interactions show that this behavior is generic, in that it holds for many models and is valid under a wide range of assumptions. Namely, if the particles are fully separated in clusters and if furthermore in a certain concentration range the chemical potential is an analytical function of the local concentration, one can take  $\mu(n) = \mu_0 + an + \dots$ . Then in lowest order in  $n$ , the interaction terms in eqs 1 and 2 are  $\alpha a n_A \nabla n_A$  and  $\alpha a n_B \nabla n_B$ , respectively. Using now eq 4 and subtracting eq 2 from eq 1, one obtains

$$\partial q / \partial t = \nabla(D + \lambda|q|)\nabla q + \xi \quad (5)$$

where  $\lambda = \alpha a$  and  $\xi(\mathbf{x}, t) = j_A(\mathbf{x}, t) - j_B(\mathbf{x}, t)$ . For the case of a strict stoichiometrical generation of particles we take the total amounts of A and B particles generated per unit time to be always equal, although the particles themselves are created randomly in space. In this case the variable  $\xi(\mathbf{x}, t)$  has the following statistical properties:

$$\langle \xi(\mathbf{x}, t) \rangle = 0 \quad (6)$$

$$\langle \xi(\mathbf{x}, t) \xi(\mathbf{x}', t') \rangle = 2j\delta(\mathbf{x} - \mathbf{x}')\delta(t - t') \quad (7)$$

Equation 5 is related to the KPZ equation for the growth of rough interfaces<sup>18</sup> but differs from it in an additional nonlinear correction to the diffusion coefficient. One can see this through an explicit application of the differential operator  $\nabla$  to the product on the right-hand side of eq 5; see ref 17. Hence eq 5 and the KPZ equation behave differently; in the limit  $\lambda \rightarrow 0$  however, both have the Edwards–Wilkinson model<sup>19</sup> as a special case.

**Long-Time Scaling Regime.** We review now quickly the scaling considerations which allow to obtain the time dependence of the concentrations at long times. These considerations (e.g., ref 17) parallel those of ref 4 for a system of particles, which, apart from reacting, do not interact with each other. Let us assume the existence of a characteristic correlation length (say, a typical cluster size)  $\Lambda(t)$ . Moreover, let us suppose that up to time  $t$  all possible reactions within each cluster of dimension  $\Lambda(t)$  have taken place. Then the total number of particles existing in the system at time  $t$  is of the order of the mean number of excess particles of one kind in each  $\Lambda(t)$  cluster. Hence we take the total number of surviving particles within a radius  $\Lambda(t)$  to be equal to the mean number of excess particles  $N_{\text{ex}}$  generated during this time within a  $\Lambda(t)$  cluster. According to Poisson statistics one has  $N_{\text{ex}} = N_t^{1/2} = (jt\Lambda(t))^{1/2}$ , where  $N_t$  is the total number of particles generated. The overall concentration is then given by

$$n(t) \sim N_{\text{ex}}/\Lambda^d \sim j^{1/2}t^{1/2}\Lambda^{-d/2}(t) \quad (8)$$

In the mean-field framework of ref 17 the behavior of  $\Lambda(t)$  for large  $t$  was obtained by going in eq 4 from the fluctuating diffusion coefficient  $D(\mathbf{x}, t) = D + \lambda|q(\mathbf{x}, t)|$  to its spatial average  $D(t) = D + 2\lambda n(t)$ . At long times and high concentrations, one can neglect  $D$  in comparison with  $2\lambda n(t)$  in the expression for the average diffusion coefficient. We obtain for the correlation length

$$\Lambda^2(t) \simeq \int_0^t D(\tau) d\tau \simeq \lambda \int_0^t n(\tau) d\tau \quad (9)$$

The system of eqs 8 and 9 is closed. To obtain from them the asymptotic behavior of the concentration  $n(t)$ , we make an ansatz in the form  $n(t) \sim j^\beta t^\gamma$  and obtain immediately

$$\gamma = \frac{2-d}{4+d} \quad (10)$$

$$\beta = \frac{2}{4+d} \quad (11)$$

In one dimension these values correspond to  $\beta = 2/5$  and  $\gamma = 1/5$ . Note that from eq 10 the upper marginal dimension  $d = 2$  follows. This finding parallels the situation in the Edwards–Wilkinson model and differs from the KPZ behavior.

The crossover from the short-time regime, eq 3, to the long-time one, in which

$$n(t) \sim j^{2/5}t^{1/5} \quad (12)$$

holds, takes place when both expressions, eqs 3 and 12, lead to the same value for  $n(t)$ . Hence the dependence of the crossover time  $t_c$  on the generation rate  $j$  is therefore in one dimension

$$t_c \sim j^{-3/4} \quad (13)$$

The corresponding crossover concentration is

$$n_c \sim j^{1/4} \quad (14)$$

These expressions will be used in analysing the numerical data.

### Numerical Simulations

**Model.** Now we consider the results of direct numerical simulations of reactions with interacting particles in one dimension. The aim of the simulations is both to assess the validity of the assumptions made in our theoretical approach and also to obtain both the behavior in the intermediate time regime and also additional information, such as correlation functions.

The simulation procedure is as follows: We consider a one-dimensional lattice of length  $L$ ;  $L$  extends normally over  $10^4$ – $10^5$  sites. The actual size of the system will always be taken such as to fulfill  $L \gg \Lambda(t_{\text{max}})$ , where  $t_{\text{max}}$  is the longest simulation time; this is in order to avoid finite-size saturation effects. Finite-size effects, which give rise to a different behavior were investigated in a related context in refs 6, 8, and 11. In our procedure A and B particles are generated pairwise and independently in space. For small values of  $j$  we generate one A and one B particle each  $k$  simulation steps (then we have  $j = (kL)^{-1}$ ); to achieve larger generation rates we create  $K$  particles of kind A and  $K$  particles of kind B per step (now  $j = KL^{-1}$ ). The diffusion of a particle in the field of the others is modeled through its jumping to one of its neighboring sites. The hopping probabilities for moving to the right (+) and to the left (−) nearest-neighbor site are

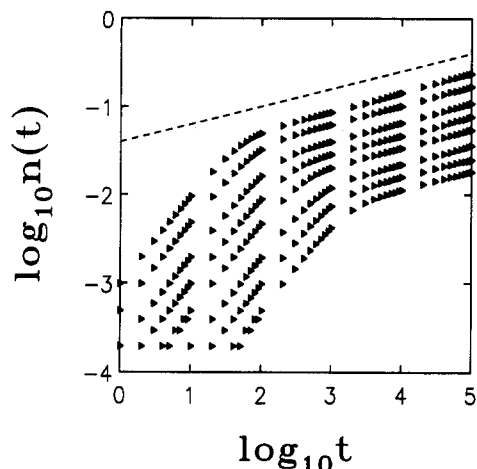
$$p_{\pm}^i = 1/2 \pm \delta_i \quad (15)$$

where the additional term  $\delta_i$  in eq 15 depends on the configuration of the surrounding particles. We have considered different situations: in the first one we restricted the interactions to the right and left neighboring particles only (these do not necessarily occupy the right and left nearest neighboring sites); in the second situation we extended the calculations to include neighbors farther away.<sup>20</sup> The simulations show that within the numerical accuracy the models belong to the same universality class, as far as exponential interactions are considered. The present results are obtained for the first situation. In this case we took

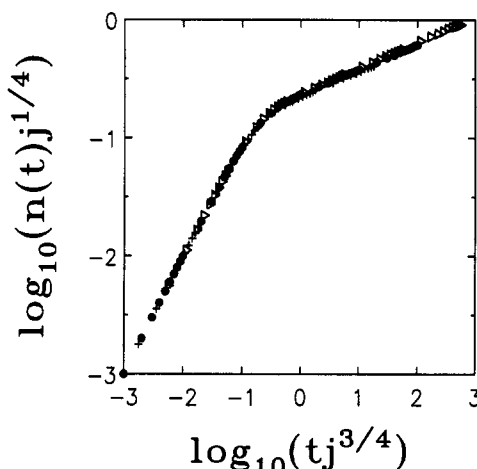
$$\delta_i = f_0 e_i [e_{i-1} \exp(-r_{i,i-1}/r_0) - e_{i+1} \exp(-r_{i,i+1}/r_0)] \quad (16)$$

where  $r_{i,j}$  are the distances between the particles  $i$  and  $j$ ,  $f_0$  and  $r_0$  are the parameters which describe the strength and range of the interaction, and the “charges”  $e_i$  are equal to +1 for the A and to −1 for the B particles. In the case of strong interactions and small distances eq 16 can lead to values of  $|\delta|$  that exceed  $1/2$ . In this case we simply put  $\delta = \pm 1/2$ : the particle moves now in the direction of the acting force with probability 1.

In Figure 1 we plot the results of the simulations for  $n(t)$  where the parameters of interaction in eq 16 were taken to be  $f_0 = 1$  and  $r_0 = 10$ . The generation rates varied between  $5 \times 10^{-6}$  and



**Figure 1.** Time dependence of the particle concentration  $n(t)$ . Note the double-logarithmic scales. The data correspond (from bottom to top) to generation rates  $j$  of  $5 \times 10^{-6}$ ,  $10^{-5}$ ,  $2 \times 10^{-5}$ ,  $5 \times 10^{-5}$ ,  $10^{-4}$ ,  $2 \times 10^{-4}$ ,  $5 \times 10^{-4}$ , and  $10^{-3}$ . See text for details.

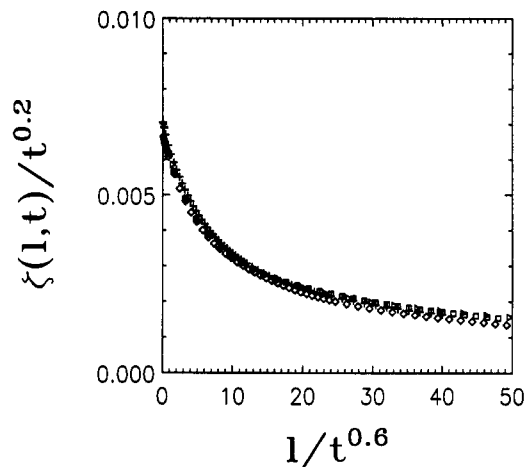


**Figure 2.** Rescaled data from Figure 1 for  $j = 10^{-5}$  (crosses),  $j = 10^{-4}$  (circles), and  $j = 10^{-3}$  (triangles). See text for details.

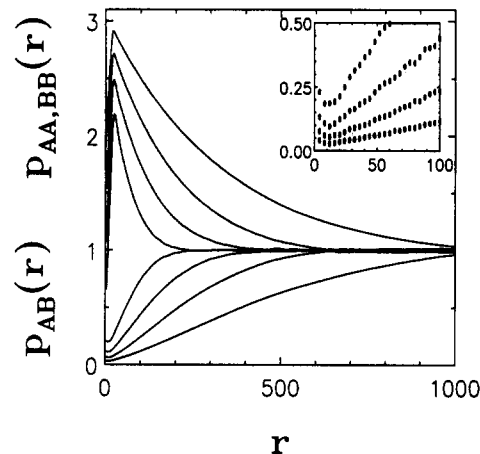
$10^{-3}$ . Each displayed curve was obtained as the average of 100 runs. The slopes in a log-log plot of Figure 1 are consistent with the short- and long-time behavior predicted by eqs 3 and 12. To prove that a one-parameter scaling relation holds, we replot in Figure 2 three of these curves (for  $j = 10^{-5}$ ,  $j = 10^{-4}$ , and  $j = 10^{-3}$ ). In Figure 2  $n(t)$  is rescaled to  $n(t)/n_c \sim n(t)j^{-1/4}$  and the time  $t$  to  $t/t_c \sim tj^{3/4}$ ; the axes are, again, double logarithmic. Note that the replotted curves collapse on the same master curve, which demonstrates the simple scaling relation proposed here.

**Cluster Structure and Correlation Functions.** Now we consider the cluster structure in the system. Note that the basic hypothesis in the theoretical consideration of the long-time regime is that particles of different kind segregate in clusters. To check this, we use here scale-dependent measures of segregation, different from the local characteristics used in refs 10 and 12. Our approach also accesses the correlation length  $\Lambda(t)$ , whose scaling behavior is our second main theoretical assumption.

Substituting eq 12  $n(t) \sim t^{1/5}$  into eq 9, we obtain that the correlation length should grow according to the power-law  $\Lambda \sim t^{3/5}$ . To prove that this is indeed the case, we consider the following: Let us take intervals of length  $l \ll L$  and calculate at time  $t$  the average  $\zeta(l, t) = \langle |N_A - N_B| \rangle / l$  over the whole system, where  $N_A$  and  $N_B$  are the numbers of A and B particles within the particular  $l$  interval. For  $l \ll \Lambda(t)$  this quantity must be of the order of the mean particle concentration (note that  $\zeta(l, t) = n(t)$ ), while for  $l \gg \Lambda(t)$ , when we have many A and B clusters within the length  $l$ ,  $\zeta(l, t) \rightarrow 0$ . Our hypothesis corresponds to the scaling of the quantity  $\zeta(l, t)/n(t) \sim \zeta(l, t)t^{-1/5}$  as a function



**Figure 3.** Behavior of  $\zeta(l, t)t^{-1/5}$  as a function of  $lt^{-3/5}$  for  $t = 300$  (triangles),  $t = 1000$  (squares),  $t = 3000$  (diamonds), and  $t = 10000$  (crosses).



**Figure 4.** Two-particle correlation functions  $p_{AA, BB}(r)$  (upper curves) and  $p_{AB}(r)$  (lower curves). The time is parametrically, from the left,  $t = 300$ ,  $t = 1000$ ,  $t = 3000$ , and  $t = 10000$ . The insert shows at higher resolution the behavior of  $p_{AB}(r)$  at short distances.

of  $l/\Lambda(t) \sim lt^{-3/5}$ . The data for  $j = 10^{-4}$  and for times  $t = 300$ ,  $1000$ ,  $3000$ , and  $10000$  are plotted in Figure 3. This figure confirms the scaling proposed.

The standard characterization of the spatial structure of the system is given by the two-particle distribution functions for particles of the same kind,  $p_{AA}(r)$  and  $p_{BB}(r)$ , and for particles of different kind,  $p_{AB}(r)$ . These are the conditional probability densities to find particles of the corresponding types at the mutual distance  $r$ , normalized over the concentration squared. Note that these quantities do not provide us with direct information about the cluster sizes, since the  $p_{XY}(r)$  depend also on the concentration profile within each cluster, which also changes with time. Now  $p_{AA}(r)$ ,  $p_{BB}(r)$ , and  $p_{AB}(r)$  are plotted in Figure 4 for the same values of time, for which  $\zeta(l, t)$  was calculated. Note that the behavior of  $p_{AB}(r)$  at small distances confirms our clusterization hypothesis: for larger times it tends to zero. The nonmonotonic behavior of  $p_{AA}(r)$  and  $p_{AB}(r)$  at small distances represents the effect of direct interactions between the particles. The peak in  $p_{AB}(r)$  corresponds to the attraction of particles of different kinds, while the behavior of  $p_{AA}(r)$  shows the ordering of the particles within a cluster due to their repulsion. In the short-range domain the distribution functions are governed by the interaction length  $r_0$  and do not scale. The overall behavior of the distribution function is not simple at all and needs further investigations. For example, the pattern near the "bifurcation", where  $p_{AA}(r)$  and  $p_{AB}(r)$  depart from each other and from unity shows scaling, whose characteristic length turns out to follow  $\Lambda'(t) \sim t^{0.5}$  rather than the form  $\Lambda \sim t^{0.6}$  obeyed by  $\zeta(l, t)$ . This can be the result of an interplay between cluster growth on one hand and the fact

that particles of the same kind order themselves inside the cluster on the other hand.

### Conclusions

We considered here analytically and numerically bimolecular reactions between particles interacting through short-range forces. We focussed on the situation of a steady particles' generation under stoichiometrical conditions. The numerical simulations confirm the theoretical conjecture that in one dimension the particles' concentration grows as  $n(t) \sim j^{2/5}t^{1/5}$  and also the underlying hypotheses about the particles' clusterization and about the behavior of the correlation length.

**Acknowledgment.** We acknowledge thankfully many helpful comments and discussions with Prof. K. Kehr, Prof. J. Klafter, Dr. G. Zumofen, and Dr. G. Oshanin. This work was supported by the Greek-German Collaboration Grant (KFA Jülich 6I3A6D01), by the SFB 60 of the DFG, and by the Fonds der Chemischen Industrie.

### References and Notes

- (1) von Smoluchowski, M. *Z. Phys. Chem.* **1917**, *92*, 129.
- (2) Ovchinnikov, A. A.; Zeldovich, Ya. B. *Chem. Phys.* **1978**, *28*, 215.

- (3) Toussaint, D.; Wilczek, F. *J. Chem. Phys.* **1983**, *78*, 2642.
- (4) Kang, K.; Redner, S. *Phys. Rev. Lett.* **1984**, *52*, 955.
- (5) Sokolov, I. M. *Zh. Eksp. Teor. Fiz.* **1988**, *94*, 199; *Sov. Phys. JETP* **1988**, *67*, 1846.
- (6) Anacker, L. W.; Kopelman, R. *Phys. Rev. Lett.* **1987**, *58*, 289.
- (7) Kopelman, R. *Science* **1988**, *241*, 1620.
- (8) Lindenberg, K.; West, B. J.; Kopelman, R. *Phys. Rev. Lett.* **1988**, *60*, 1777.
- (9) Schnörer, H.; Kuzovkov, V.; Blumen, A. *Phys. Rev. Lett.* **1989**, *63*, 805.
- (10) West, B. J.; Kopelman, R.; Lindenberg, K. *J. Stat. Phys.* **1989**, *54*, 1429.
- (11) Clément, E.; Sander, L.; Kopelman, R. *Phys. Rev. A* **1989**, *39*, 6455.
- (12) Harmon, L. A.; Li, L.; Anacker, L. W.; Kopelman, R. *Chem. Phys. Lett.* **1989**, *163*, 463.
- (13) Sokolov, I. M.; Schnörer, H.; Blumen, A. *Phys. Rev. A* **1991**, *44*, 2388.
- (14) Zumofen, G.; Klafter, J.; Blumen, A. *J. Stat. Phys.* **1991**, *65*, 1015; *Phys. Rev. A* **1991**, *44*, 8390.
- (15) Debye, P. *J. Electrochem. Soc.* **1942**, *82*, 265.
- (16) Kuzovkov, V.; Kotomin, E. *J. Chem. Phys.* **1993**, *98*, 9107.
- (17) Sokolov, I. M.; Blumen, A. *Europhys. Lett.* **1993**, *21*, 855.
- (18) Kardar, M.; Parisi, G.; Zhang, Y.-C. *Phys. Rev. Lett.* **1986**, *56*, 889.
- (19) Edwards, S. F.; Wilkinson, D. R. *Proc. R. Soc. London A* **1982**, *A381*, 17.
- (20) Sokolov, I. M.; Argyrakis, P.; Blumen, A., *Fractals* **1993**, *1*, 470.