The Diffusion-Limited Reaction A + B → 0 on a Fractal Substrate

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We show in this paper how the segregation of reactants in the diffusion-limited reaction A + B → 0 on a fractal substrate arises. For spectral dimensions $d_s \leqslant 2$ we obtain segregation controlled by the source and/or the intrinsic lifetime of the particles.

KEY WORDS: Diffusion; reaction; self-organization; fractals.

1. SEGREGATION IN LOW-DIMENSIONAL KINETICS

The reaction A + B → 0 is of great practical and conceptual importance in solid-state chemistry and physics.[1] It describes the annihilation kinetics of electrons with holes and the annihilation of defects with antidefects in crystals[2] and also certain catalytic reactions, which often take place on substrates with complex geometries. Ovchinnikov and Zeldovich[4] and Toussaint and Wilcek[5] demonstrated the existence of a large-scale self-organization phenomenon known as *segregation* during the decay of reactants in A + B → 0 from a random initial state. Instead of a random mixture, after a long time the distribution consists of large patches of A or B. This is easily understood as the amplification of initial statistical fluctuations in the densities of the reactants: the local majority survives.

A much more surprising segregation effect was demonstrated numerically by Anacker and Kopelman[10] in the steady state, where one might have expected the effect to be averaged out by the random external source.

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The point is that for-low dimensional or fractal substrates diffusion is inefficient in averaging fluctuations. Several theoretical studies followed.[11-17] We analyzed[15,16] the problem in Euclidean spaces for particles of finite radius. Our results reduce, in the limit of zero size, to the results of Lindenberg *et al.*[12] and of Ben-Avraham and Doering,[13] but not those of Zhang.[11] The critical dimension of the problem seems to be 2, different from the value $d_c = 4$ for the transient problem.[11] Here we propose a scheme to investigate the segregation for fractal structures. The essential problem here is to account properly for the balance of diffusion, reaction, and the incoming flux.

We must set up the problem with some care: for the Euclidean case we showed that[15,16] the results, and the existence of segregation, are very much dependent on the details of the source that we assume. For example, if we assume that annihilation cannot take place with the incoming flux, then another instability, the well-known effect of *poisoning*, occurs: in this case the random wandering of the difference $N_A - N_B$ eventually sticks at one of the two stable points corresponding to all A or all B. In order to avoid this, and to have a well-defined thermodynamic limit, we assume either *vertical annihilation*, i.e., that an incoming particle reacts directly with an unlike particle if it happens to land on the same site, or *desorption*, where there is a finite probability of spontaneous emptying of a filled site. In either case, there is a mean lifetime τ for each particle, and the poisoned states are no longer stable. If R is the density of particles A (or B) arriving per unit time, then for the vertical annihilation case $\tau = Rv$, where v is the volume per site. For desorption, where we consider the reactions $A \rightarrow 0$ and $B \rightarrow 0$ with the same rate Γ in addition to the $A + B \rightarrow 0$ reaction, clearly, $\Gamma = 1/\tau$.

We now seek to derive the macroscopic rate law and the scale of the segregation. We will do this with an approach based on correlation functions of the densities.

2. CORRELATION FUNCTION APPROACH

We have discussed these problems for reactions on Euclidean substrates.[15,16] Our major results can be qualitatively understood as follows. Consider, instead of the local particle densities $\rho_A(\mathbf{r}, t)$ and $\rho_B(\mathbf{r}, t)$, the quantities $\rho(\mathbf{r}, t) = \rho_A(\mathbf{r}, t) + \rho_B(\mathbf{r}, t)$, $\gamma(\mathbf{r}, t) = \rho_A(\mathbf{r}, t) - \rho_B(\mathbf{r}, t)$ and the correlation function $m(r, t) = \langle \gamma(\mathbf{x}, t) \gamma(\mathbf{x} + \mathbf{r}, t) \rangle$.

Now suppose that there is segregation over some scale Λ. There will be patches of typical size Λ which are either all A or all B. In the interior of these patches $m(a) \cong \rho^2$, where $\rho = \langle \rho(\mathbf{r}, t) \rangle$ and a is the molecular

radius. Further, since on scale Λ the sign of m should reverse, we can estimate

$$|\nabla m|_a \approx \rho^2/\Lambda \tag{1}$$

Now part of m is related to the reaction rate Q. Note that

$$Q = D \int_{\Sigma} d\mathbf{S} \, \nabla \langle \rho_A(\mathbf{x}, t) \, \rho_B(\mathbf{x} + \mathbf{r}, t) \rangle \tag{2}$$

Here D is the diffusion coefficient, Σ the cross section of the molecule, and $Q = R(1 - v\rho)$ is the bimolecular reaction rate taking into account the excluded volume v. The reaction rate represents the disappearance of particles at the "black sphere" radius a, and the correlation function inside the integral is the part of m which accounts for the reaction. We will shortly have occasion to write a diffusion equation for m. To take the reaction part into account, we must set a boundary condition on the discontinuity of the flux of m which matches Eq. (2):

$$\Lambda \cdot (\nabla m|_a) = -Q/\Sigma D \tag{3a}$$

From (1) this implies

$$Q \approx \Sigma D \rho^2/\Lambda \tag{3b}$$

Now the balance of fluxes for $m(\mathbf{r})$ is, for $r \geqslant a$,

$$\partial m/\partial t = D\nabla^2 m - m/\tau + [Q/\Sigma] \, \delta_{r-a} \tag{4}$$

where we have added a diffusion, lifetime, and reaction term. We have solved this equation in the steady state, for which $\partial m/\partial t = 0.$[15,16]

3. FRACTAL SUBSTRATES

We now consider a fractal substrate embedded in a Euclidean space of dimension d with a fractal dimension d_f and a spectral dimension d_s with a short-distance cutoff at scale a. In such a medium it is well known that a random walk obeys $r^{d_w} \sim t$, where $d_w = 2d_f/d_s$. In order to take this into account, we generalize Eq. (4), and use the fractal diffusion operator of O'Shaugnessy and Procaccia.[18-20] The fractal medium is viewed as an effective medium with anomalous properties contained in two parameters, the anomalous diffusion exponent $\theta = 2(d_f/d_s - 1)$ and the generalized Fick

coefficient K. We interpret $m(\mathbf{r})$ to be the analytic envelope of the correlation function for each realization and we replace Eq. (4) by:[18]

$$\hat{O}m - m/\tau + [Q/\Sigma]\,\delta_{r-a} = 0$$

$$\hat{O} = K\frac{1}{r^{d_f-1}}\frac{\partial}{\partial r}\left[r^{d_f-1-\theta}\frac{\partial}{\partial r}\right] \tag{5}$$

This operator accounts for diffusion in an isotropic effective medium. We define the microscopic diffusion constant to be $D = Ka^{-\theta}$. Note also that this averaged approach works[19] only for sites that are repeatedly visited by the diffusing particles, i.e., $r^{d_w} \ll t$. We will return to this point below.

If $\tau = \infty$, the only acceptable solution is $m(r) = \text{const}$, under the condition $Q = 0$, namely *saturation* of the system in one of the species. For finite lifetime Eq. (5) has a solution in modified Bessel functions. For $r > a$, the solution is

$$m(r) = A\left(\frac{r}{a}\right)^{\beta v}\frac{\mathbf{K}_v[(a/\beta\xi)(r/a)^\beta]}{\mathbf{K}_v(a/\beta\xi)} \tag{6}$$

where $\mathbf{K}_v(z)$ is a modified Bessel function, and where $\beta = d_w/2$, $\xi = (D\tau)^{1/2}$, and $v = 1 - d_s/2$. Here A is a constant to be determined by the slope discontinuity. Thus,

$$A = m(a) = \frac{Q\xi}{D\Sigma_{d_f}}\frac{\mathbf{K}_v(a/\beta\xi)}{\mathbf{K}_{1-v}(a/\beta\xi)} \tag{7}$$

Putting together Eq. (7) and Eq. (3b), we obtain a segregation length:

$$\Lambda = \xi\frac{\mathbf{K}_v(a/\beta\xi)}{\mathbf{K}_{1-v}(a/\beta\xi)} \tag{8}$$

This equation along with Eq. (3b) defines a rate law for spectral dimensions $1 \leqslant d_s \leqslant 2$, which interpolates between Euclidean cases for $d_f = d_s = 1$ and $d_f = d_s = 2$.[15,16] After an expansion in a/ξ, we obtain the two following regimes:

(i)   For low density, $\xi/a \gg e^{1/(2-d_s)}$, we have

$$\Lambda \sim \tau^{1-d_s/2} \tag{9}$$

For the vertical annihilation case we obtain a limiting scaling behavior for the reaction law:

$$R \sim Q \sim \rho^2/\Lambda \sim \rho^2/[Rv]^{1-d_s/2}$$

$$Q \sim \rho^{4/d_s} \tag{10}$$

Therefore, we find an anomalous order of reaction $X = 4/d_s$ that generalizes the one found for $d = 1$ ($X = 4$).[15] For the desorption case the reaction order remains classical ($X = 2$), since τ is constant. The condition

$\xi/a \gg e^{1/(2-d_s)}$ is a reasonable approximation in the case of percolation clusters ($d_s = 4/3$). It corresponds to an external source rate $R < 2 \times 10^{-2}$.

(ii) For $1 \ll \xi/a \ll e^{1/(2-d_s)}$ and in the vertical annihilation case, there is no simple scaling expression for the rate law. It is important to notice that, for symmetric desorption, though a mesoscopic segregation is present, a classical rate law ($X = 2$) is obtained.

Now we test these predictions in the vertical annihilation case using Monte Carlo simulations on a percolation cluster. The value of the generalized Fick coefficient K is determined *independently* by Monte Carlo simulations of the mean square displacement of a random walker. For a "myopic ant"[21] algorithm we have $K = 0.377 \pm 0.004$. The reaction surface Σ is the average number of sites-nearest-neighbors. For the percolation cluster, we numerically calculated $\Sigma = 2.52 \pm 0.02$. Thus, the theoretical reaction law has *no* adjustable parameters. In Fig. 1 we show the results of simulations on the largest cluster for a 100×100 square lattice at criticality ($p = 0.59$). The agreement between theory and simulations is good and, as predicted earlier, the deviation from the scaling behavior with an exponent for the order of reaction $X = 4/d_s = 3$ occurs at very high densities ($\rho > 2 \times 10^{-1}$ and $R > 2 \times 10^{-2}$). These results justify *a posterori* the use of Eq. (5) in the fractal case.

4. VALIDITY OF THE APPROXIMATION

In order to use the diffusion operator in the form that we have given, we need[19] $r \ll t^{1/d_w}$. Now the relevant time for any particle is τ, and the relevant length is $\Lambda \sim \tau^{1-d_s/2}$. Thus we need

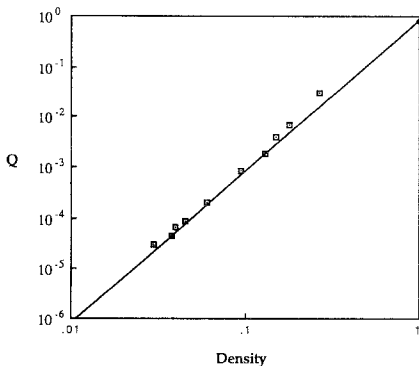$$\tau^{1-d_s/2} \ll \tau^{1/d_w}, \qquad d_w(1-d_s/2) < 1 \tag{11}$$

Fig. 1. Computer simulations compared to theoretical expectations on a percolation cluster. The curve is the low-density asymptotic behavior showing an effective order of reaction $X = 4/d_s$.

This exponent inequality is satisfied for a 2D percolation cluster and Sierpinski gasket, but not for a 3D percolation cluster. The consequences of this violation are not clear at the moment.

5. CONCLUSIONS

In conclusion, this paper shows how the segregation of reactants for the reaction $A + B \to 0$ at steady state on a fractal can be understood. For a spectral dimension smaller than 2, segregation occurs in the medium up to scales determined by the source or by the intrinsic lifetime of the particles. This phenomenon does *not* occur in higher dimensions: we have previously[15,16] shown that $\Lambda \sim \ln(\tau)$ in $d = 2$, and $\Lambda \sim a$ for $d > 2$. The case of vertical annihilation exhibits an anomalous exponent for the order of reaction $(X = d_s/4)$, due to a source-dependent scale of segregation.

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REFERENCES

1. R. Kopelman, *Science* **241**:1620 (1988).
2. V. Kuzovkov and E. Kotomin, *Phys. Stat. Sol. (b)* **105**:789 (1981).
4. A. A. Ovchinnikov and Y. B. Zeldovich, *Chem. Phys.* **28**:215 (1978).
5. D. Toussaint and F. Wilczek, *J. Chem. Phys.* **78**:2642 (1983).
6. K. Kang and S. Redner, *Phys. Rev. Lett.* **52**:955 (1984).
7. M. Bramson and J. L. Leibowitz, *Phys. Rev. Lett.* **61**:2397 (1988).
8. K. Kang and S. Redner, *Phys. Rev. A* **32**:435 (1985).
9. P. Meakin and H. E. Stanley, *J. Phys. A* **17**:L173 (1984).
10. L. W. Anacker and R. Kopelman, *Phys. Rev. Lett.* **58**:289 (1987).
11. Z. Y. Zhang, *Phys. Rev. Lett.* **59**:1726 (1987).
12. K. Lindenberg, B. West, and R. Kopelman, *Phys. Rev. Lett.* **60**:1777 (1988).
13. D. Ben-Avraham and C. Doering, *Phys. Rev. A* **37**:5007 (1988).
14. S. Kanno, preprint (1988).
15. E. Clément, L. M. Sander, and R. Kopelman, *Phys. Rev. A* **39**:6455 (1989).
16. E. Clément, L. M. Sander, and R. Kopelman, *Phys. Rev. A* **39**:6466 (1989).
17. I. M. Sokolov, *Phys. Lett. A* **139**:403 (1989).
18. B. O'Shaughnessy and I. Procaccia, *Phys. Rev. A* **32**:3073 (1985).
19. S. Havlin and D. Ben-Avraham, *Adv. Phys.* **36**:695 (1987).
20. E. Clément, L. M. Sander, and R. Kopelman, *Phys. Rev. A* **39**:6472 (1989).
21. D. Stauffer, *Introduction to Percolation Theory* (Taylor and Francis, London, 1985).