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Diffusion-controlled annihilation $A+B\rightarrow 0$ with initially separated reactants: The death of an A particle island in the B particle sea

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We consider the diffusion-controlled annihilation dynamics $A+B\rightarrow 0$ with equal species diffusivities in the system where an island of particles A is surrounded by the uniform sea of particles B. We show that once the initial number of particles in the island is large enough, then at any system's dimensionality d the death of the majority of particles occurs in the *universal scaling regime* within which $\approx 4/5$ of the particles die at the island expansion stage and the remaining $\approx 1/5$ at the stage of its subsequent contraction. In the quasistatic approximation, the scaling of the reaction zone has been obtained for the cases of mean-field ($d\geqslant d_c$) and fluctuation ($d<d_c$) dynamics of the front.

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The reaction front formed in the $A+B\rightarrow 0$ reaction-diffusion systems with initially separated reactants is of great interest since it represents a pattern for a wide spectrum of processes in physics, chemistry, and biology [1]. Since the seminal paper of Galfi and Racz [2] much work has been devoted to studying this problem by different approaches [3–20]. A standard way to treat the problem analytically is to solve the system of equations

$$\partial a/\partial t = D_A \nabla^2 a - R, \quad \partial b/\partial t = D_B \nabla^2 b - R \tag{1}$$

with the initial state given by

$$a(x,0) = a_0 \theta(-x), \quad b(x,0) = b_0 \theta(x), \tag{2}$$

where $a(x,t)$ and $b(x,t)$ are the mean local concentrations of A's and B's, $R(x,t)$ is the macroscopic reaction rate and $\theta(x)$ denotes the Heaviside step function, so that the A's are initially uniformly distributed on the left side ($x<0$), and the B's on the right side ($x>0$) of the initial boundary.

Dimensional [9,14] and renormalization group [11,12] analyses show that at $d\geqslant d_c=2$ one can adopt the mean-field approximation $R(x,t)=ka(x,t)b(x,t)$ (k being the reaction rate constant) with logarithmic corrections in the $2d$ case, whereas in $1d$ systems fluctuations play the dominant role and the explicit form of R remains unknown. There are, however, several techniques which enable one to derive a lot of information from Eq. (1) even for $d<d_c$. They are focused on the long-time limit $kt\rightarrow\infty$ and include, as two basic concepts, the scaling ansatz, [2] and the quasistatic approximation [8,9,11]. According to the scaling ansatz, the long-time behavior of the system inside the reaction zone may be represented in the form

$$R = R_f \mathcal{Q}\left(\frac{x-x_f}{w}\right), \tag{3}$$

where $x_f \propto t^{1/2}$ denotes the position of the reaction zone center, $R_f \propto t^{-\beta}$ is the height, and $w\propto t^{\alpha}$ is the width of the reaction zone. At $d\geqslant d_c$ the scaling exponents take the values $\alpha=1/6, \beta=2/3$ [2], whereas at $d=1$ they appear to be equal to $\alpha=1/4, \beta=3/4$ [9–14], so that at any d the width of the reaction zone on the diffusion length scale $\Lambda_D \propto t^{1/2}$ asymptotically unlimitedly contracts:

$$w/\Lambda_D \rightarrow 0 \quad \text{as} \quad t\rightarrow\infty.$$

The quasistatic approximation (QSA) consists in the assumption that for sufficiently long times the kinetics of the front is governed by two characteristic time scales. One time scale $t_J = -(d\ln J/dt)^{-1}$ controls the rate of change in the diffusive current $J=J_A=J_B$ of particles arriving at the reaction zone. The second time scale $t_f \propto w^2/D$ is the equilibration time of the reaction front. Assuming $t_f/t_J \ll 1$ from the QSA in the mean-field case with $D_{A,B}=D$, it follows [8,9]

$$R_f \sim J/w, \quad w\sim (D^2/Jk)^{1/3}, \tag{4}$$

whereas in the $1d$ case w acquires the k-independent form $w\sim (D/J)^{1/2}$ [9,11,17]. The most important feature of the QSA is that w and R_f depend on t only through the time dependent boundary current $J(t)$, which can be calculated analytically without knowing the concrete form of $\mathcal{Q}$, i.e., in fact, representing the reaction zone on the scale Λ_D in the form $R(x,t)=J\delta(x-x_f)$. On the basis of the QSA the general description of spatiotemporal behavior of the system $A+B\rightarrow 0$ has been obtained for arbitrary nonzero diffusion coefficients and initial species concentrations [19]. These results are in full agreement with extended numerical calculations and experiments and were generalized recently to the cases of reversible reaction $A+B\leftrightarrow C$ [21–24] and to several more complex reactions [25–29].

Until now, however, the main attention has been focused on the systems with A and B domains having an unlimited extension, i.e., with unlimited number of A's and B's particles. The aim of this work is to develop *a new line* in the study of the $A+B\rightarrow 0$ dynamics under the assumption that the particle number of one of the species, say A, per unit of the initial boundary is finite. More precisely, we will consider the problem on the dynamics of death of an A particle island surrounded by the uniform sea of particles B and will reveal the defining features of this process.

Let particles A with concentration a_0 be uniformly distributed in the island $x\in(-L,L)$ surrounded by the unlimited

sea of particles B with concentration b_0 on the left $x\in(-\infty,-L)$ and on the right $x\in(L,\infty)$ of the island. By symmetry, our problem is reduced to the solution of system (1) in the interval $x\in[0,\infty)$ at the initial conditions

$$a(x,0)=a_0\theta(L-x),\quad b(x,0)=b_0\theta(x-L)$$

with the boundary conditions

$$\nabla(a,b)|_{x=0}=0,\quad b(\infty,t)=b_0.$$

To simplify the problem essentially we will assume, as usually, $D_A=D_B=D$. Then by measuring the length, time, and concentration in units of L, L^2/D, and b_0, respectively, i.e., assuming $L=D=b_0=1$, and defining the difference concentration $s(x,t)=a(x,t)-b(x,t)$ and the ratio of initial concentrations $a_0=r$, we come from Eq. (1) to the simple diffusion equation

$$\partial s/\partial t=\nabla^2 s \tag{5}$$

with the initial conditions

$$s_0(x\in[0,1))=r,\quad s_0(x\in(1,\infty))=-1,$$

and the boundary conditions

$$\nabla s|_{x=0}=0,\quad s(\infty,t)=-1.$$

The solution to Eq. (5) has the form

$$s(x,t)=\frac{r+1}{2}\left[\operatorname{erf}\left(\frac{1+x}{2\sqrt{t}}\right)+\operatorname{erf}\left(\frac{1-x}{2\sqrt{t}}\right)\right]-1, \tag{6}$$

whence, according to condition $s(x_f,t)=0$ [2,19], there immediately follows the equation defining the law of motion of the reaction front center, $x_f(t)$:

$$\operatorname{erf}\left(\frac{1+x_f}{2\sqrt{t}}\right)+\operatorname{erf}\left(\frac{1-x_f}{2\sqrt{t}}\right)=\frac{2}{r+1}. \tag{7}$$

Let us assume that $d\geqslant d_c$ and the reaction rate constant k is sufficiently large [30] so that at times $t\sim t_{GR}\propto k^{-1}\ll 1$ the annihilation goes to the scaling Galfi-Racz regime, i.e., in the vicinity of x_f there forms a narrow reaction zone $w/\Lambda_D\ll 1$. At $t\ll 1$ and $|1-x_f|\ll 1$ from Eq. (7) in accordance with Ref. [2] we find

$$x_f=1+c_f\sqrt{t}+\cdots,$$

where $\operatorname{erf}(c_f/2)=(r-1)/(r+1)$ and, hence, at $r\leqslant 1$ the island contracts, whereas at $r>1$ the island expands. By virtue of the fact that the number of particles in the island (per unit of the initial boundary) is finite, the stage of its expansion always goes to the stage of its subsequent contraction to end in an instant of time t_c, when the reaction front center approaches the origin of coordinates, $x_f(t_c)=0$:

$$\operatorname{erf}(1/2\sqrt{t_c})=1/(r+1). \tag{8}$$

According to Eq. (8) at $r\gg 1$ the "lifetime" of the island $t_c\gg 1$, so the majority of the particles die at times $t\gg 1$, when the diffusive length exceeds appreciably the initial island size, $\Lambda_D\gg 1$. The evolution of the island in such a large-t regime is of principal interest to us here, and its analysis is the main goal of the present paper.

In the limit $r,t\gg 1$ from Eq. (6) we find

$$s(x,t)=\frac{(r+1)}{\sqrt{\pi t}}e^{-x^2/4t}(1-\chi)-1, \tag{9}$$

where $\chi=(1-x^2/2t)/12t+\cdots$, and, hence, the law of the front motion is

$$x_f=2\sqrt{t}(1+\epsilon)\ln^{1/2}\left[\left(\frac{r+1}{\sqrt{\pi t}}\right)(1-\epsilon)\right], \tag{10}$$

where $\epsilon=1/12t+\cdots$. By assuming $t\gg 1>t_{GR}$, at the stage of the island expansion and at a considerable time period of its subsequent contraction, the duration of which will be estimated below, the reaction zone width is $w\ll x_f<\Lambda_D$, therefore in terms of the QSA we can take $w/x_f\to 0$, and, hence, $R(x,t)=J\delta(x-x_f)$ so that $a=s,b=0$ when $x<x_f$, and $a=0,b=|s|$ when $x>x_f$. Thus, by neglecting the width of the reaction zone, for the number of particles in the island we have $N(t)=\int_0^{x_f}a(x,t)dx=\int_0^{x_f}s(x,t)dx$ whence, with account taken of Eq. (9) and neglecting the contribution of χ, we find

$$N(t)=(r+1)\operatorname{erf}(x_f/2\sqrt{t})-x_f. \tag{11}$$

Let us now calculate the maximal amplitude x_f^M of the island expansion and the time t_M of its achievement. According to Eq. (7), for $r>1$ from condition $\dot{x}_f=0$ we have exactly

$$x_f^M=2t_M\,\operatorname{arccoth}(x_f^M),$$

whence for $r\gg 1$ it follows

$$x_f^M=\sqrt{2t_M}(1+1/12t_M+\cdots). \tag{12}$$

Neglecting the terms $O(1/r^2)$, from Eqs. (10) and (12) we find

$$t_M=(r+1)^2/\pi e,\quad x_f^M=(r+1)\sqrt{2/\pi e}.$$

Comparing t_M with the lifetime of island (8),

$$t_c=(r+1)^2/\pi,$$

we conclude that independently of r the ratio $t_c/t_M=e=\text{const}$. Going with allowance for this to the reduced coordinate $\zeta=x/x_f^M$ and time $\tau=t/t_c$ we, finally, come to scaling relations for the distribution of particles $s(\zeta,\tau)$,

$$s(\zeta,\tau)=e^{-\zeta^2/2e\tau}/\sqrt{\tau}-1, \tag{13}$$

for the center of the reaction front,

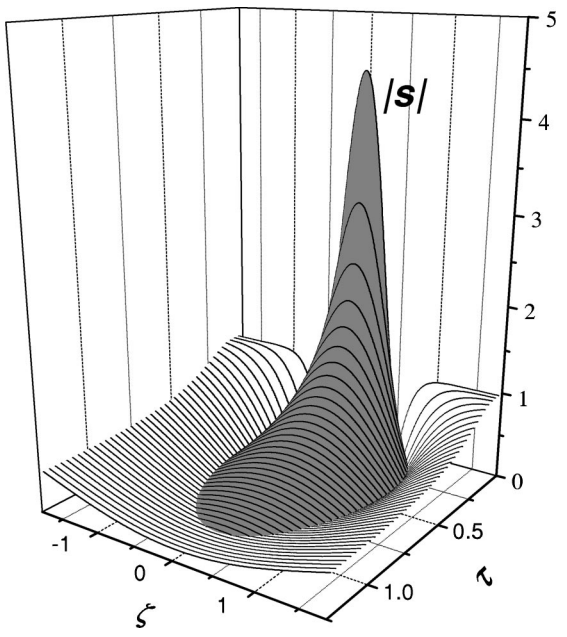

FIG. 1. Evolution of the distribution of particles $|s(\zeta,\tau)|$ calculated according to Eqs. (6) and (7) for $r=10$. The left part of the distribution ($\zeta<0$) is obtained through the mirror reflection of the right one ($\zeta>0$). The region $s>0$ ($-\zeta_f<\zeta<\zeta_f$), belonging to the island, is colored gray. For demonstration only a part of the picture is shown for $\tau>0.03$.

$$\zeta_f=\sqrt{e\tau|\ln\tau|}, \tag{14}$$

and for the number of particles in the island,

$$N/N_0=\gamma_r\mathcal{G}(\tau), \tag{15}$$

where $\gamma_r=(r+1)/r\rightarrow 1$ as $r\rightarrow\infty$ and scaling function

$$\mathcal{G}(\tau)=\mathrm{erf}(\sqrt{|\ln\tau|/2})-\sqrt{2\tau|\ln\tau|/\pi}.$$

From Eqs. (13) and (15) we find that in the turning point $\tau_M=1/e$,

$$a(0,\tau_M)=\sqrt{e}-1=0.648\,72\ldots,$$

$$\gamma_r^{-1}N_M/N_0=0.198\,86\ldots,$$

and, hence, independently of the initial number of particles, $N_0=r$, $\approx 4/5$ of the particles die at the stage of the island expansion and the remaining $\approx 1/5$ at the stage of its subsequent contraction. In Figs. 1 and 2 are shown the calculated, according to Eqs. (6) and (7), plots of the behavior of the particle distribution $|s(\zeta,\tau)|$, of the center of the reaction front, $\zeta_f(\tau)$, and the number of particles $\gamma_r^{-1}N(\zeta_f)/N_0$, which give the full insight into the scaling regime of the death of islands (13)–(15).

Let us come now to the question of the scaling behavior of the reaction rate $R(x,t)$ in the vicinity of the reaction front center x_f. Assuming according to Refs. [8,9,19] that within the applicability of the inequalities $t_f/t_J\ll 1$ and $w\ll x_f$ the reaction rate $R(x,t)$ can be described in terms of the QSA by Eqs. (3) and (4) to calculate R_f and w, it only remains for us

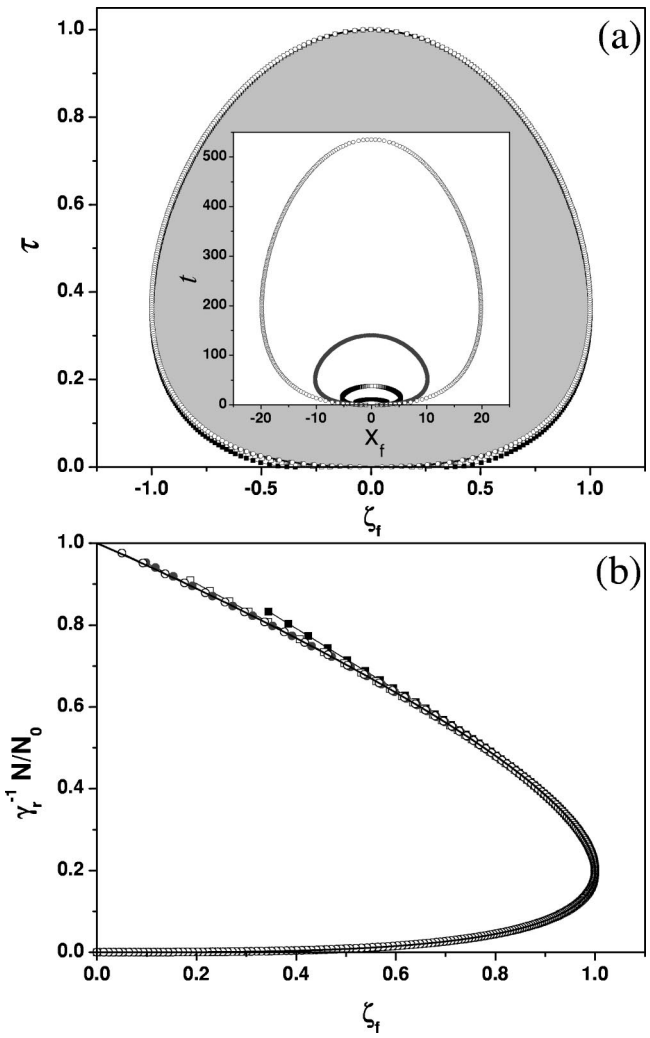

FIG. 2. (a) Inset: Time dependences $x_f(t)$ calculated from Eq. (7) at $r=5$ (filled squares), $r=10$ (open squares), $r=20$ (filled circles), and $r=40$ (open circles). Main panel: Collapse with the growing r of the shown, in the inset, dependences to the scaling law (14) (solid line) in the rescaled coordinates $\zeta_f(\tau)$. For completeness is shown the motion of the both island fronts: $\pm x_f(t),\pm\zeta_f(\tau)$. (b) Collapse with the growing r of the calculated, from Eqs. (6) and (7), dependences of the reduced particle number in the island $\gamma_r^{-1}N/N_0$ vs ζ_f to the scaling function $\mathcal{G}(\zeta_f)$ (solid line): $r=5$ (filled squares), $r=10$ (open squares), $r=20$ (filled circles), and $r=40$ (open circles). The number of the island particles, N, has been calculated by integrating Eq. (6) from 0 to x_f on assuming that $w/x_f\rightarrow 0$.

to calculate the diffusive current $J(t)$ of particles arriving at the reaction zone. According to Eqs. (9) and (11), we have

$$J=-\dot{N}=-\partial s/\partial x|_{x=x_f}=x_f/2t,$$

whence it follows

$$J/J_M=\sqrt{|\ln\tau|/e\tau}, \tag{16}$$

where $J_M=1/x_f^M=\sqrt{\pi e/2}/(r+1)$. Substituting Eq. (16) into Eqs. (4) we come to the scaling of the reaction zone,

$$R_f \sim (J^4 k)^{1/3} = R_f^M \left(\frac{|\ln \tau|}{e\tau} \right)^{2/3}, \tag{17}$$

$$w \sim (Jk)^{-1/3} = w_M \left(\frac{e\tau}{|\ln \tau|} \right)^{1/6}, \tag{18}$$

where $R_f^M \sim (k/r^4)^{1/3}$ and $w_M \sim (r/k)^{1/3}$ so that $wR_f \sim R_{global} = \int_0^\infty R dx = J$. From Eq. (18) it is seen that at the stage of the island contraction the logarithmic term becomes dominant, and as $\tau \to 1$, i.e., $\delta\tau = 1 - \tau \to 0$, the width of the reaction front w diverges as $w \propto (\delta\tau)^{-1/6}$. Comparing the characteristic times $t_J = -(d \ln J/dt)^{-1} \sim r^2 \delta\tau$ and $t_f \sim w^2 \sim (r/k)^{2/3} (\delta\tau)^{-1/3}$ we have $t_f/t_J \sim (r^2 k)^{-2/3} (\delta\tau)^{-4/3}$, whence it follows that the characteristic time at which the QSA is violated is

$$\delta\tau_Q \propto 1/r\sqrt{k}.$$

Comparing then w and x_f we obtain $w/x_f \sim \sqrt{t_f/t_J} \sim (r^2 k)^{-1/3} (\delta\tau)^{-2/3}$, whence it follows that the width of the reaction zone becomes comparable with the island size at the times

$$\delta\tau_w \sim \delta\tau_Q \propto 1/r\sqrt{k}. \tag{19}$$

From Eq. (19) it is seen that at sufficiently large values of $k \gg 1$ the characteristic times $\delta\tau_w \sim \delta\tau_Q \ll 1/r \ll 1$ and, hence, practically all the particles die in the scaling regime (15).

The analogous estimations in the case of the k-independent fluctuation $1d$ regime with $w \sim 1/\sqrt{J}$ yield expressions (17) and (18) with $R_f^{MF} \sim r^{-3/2}, w_M^F \sim \sqrt{r}$, and exponents 3/4 instead of 2/3, and 1/4 instead of 1/6, respectively. In the end, for the $1d$ case we have

$$\delta\tau_w^F \sim \delta\tau_Q^F \propto 1/r^{2/3}. \tag{20}$$

According to Eq. (20), despite the much more "blurred" structure of the $1d$ island, in this case, too, in the limit of sufficiently large $r \gg 1$ the majority of the particles die in the scaling regime (15).

In summary, the problem of the death of an A particle island in the B particle sea at equal diffusivities of A's and B's particles has been first considered. It has been found that at sufficiently large initial number of particles in the island, $r \gg 1$, and sufficiently large reaction rate constant, $k \gg 1$, the death of the majority of the particles at any d occurs in the universal scaling regime, and the most essential features of this regime have been revealed. The obtained results can have many applications, especially in surface science, and, in particular, they can provide fresh insight into the dynamics of the Ovchinnikov-Zeldovich hierarchic A-B structures [1]. By analogy with Ref. [19] it may be expected that the analysis presented can be easily extended over the general case $D_A \neq D_B \neq 0$ (note that in the static case $D_B = 0$, which belongs to the separate universality class, with initially N_0 particles A at the origin of coordinates, in Ref. [16] the scaling formally coincident with Eq. (15), $N = N_0 \mathcal{F}(t/N_0^2)$, was found). An investigation into the general case of nonzero diffusivities and a most interesting generalization for the anisotropic diffusion of reactants are expected to be presented in a future report.

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[1] D. ben Avraham and S. Havlin, *Diffusion and Reactions in Fractals and Disordered Systems* (Cambridge University Press, Cambridge, 2000); B. Chopard and M. Droz, *Cellular Automata Modeling of Physical Systems* (Cambridge University Press, Cambridge, 1998).
[2] L. Galfi and Z. Racz, Phys. Rev. A **38**, 3151 (1988).
[3] Z. Jiang and C. Ebner, Phys. Rev. A **42**, 7483 (1990).
[4] H. Taitelbaum *et al.*, J. Stat. Phys. **65**, 873 (1991).
[5] S. Cornell *et al.*, Phys. Rev. A **44**, 4826 (1991).
[6] H. Larralde *et al.*, Phys. Rev. A **46**, 855 (1992).
[7] M. Araujo *et al.*, Phys. Rev. Lett. **68**, 1791 (1992).
[8] E. Ben-Naim and S. Redner, J. Phys. A **28**, L575 (1992).
[9] S. Cornell and M. Droz, Phys. Rev. Lett. **70**, 3824 (1993).
[10] M. Araujo *et al.*, Phys. Rev. Lett. **71**, 3592 (1993).
[11] B.P. Lee and J. Cardy, Phys. Rev. E **50**, R3287 (1994); J. Stat. Phys. **80**, 971 (1995).
[12] M. Howard and J. Cardy, J. Phys. A **28**, 3599 (1995).
[13] S. Cornell, Phys. Rev. Lett. **75**, 2250 (1995); Phys. Rev. E **51**, 4055 (1995).
[14] P.L. Krapivsky, Phys. Rev. E **51**, 4774 (1995).
[15] M. Hoyuelos *et al.*, J. Phys. A **28**, L483 (1995).
[16] S. Havlin *et al.*, Physica A **221**, 1 (1995).
[17] G.T. Barkema *et al.*, Phys. Rev. E **53**, R2017 (1996).
[18] Z. Koza and H. Taitelbaum, Phys. Rev. E **54**, R1040 (1996).
[19] Z. Koza, J. Stat. Phys. **85**, 179 (1996).
[20] M.A. Rodriquez and H.S. Wio, Phys. Rev. E **56**, 1724 (1997).
[21] B. Chopard *et al.*, Phys. Rev. E **47**, R40 (1993).
[22] M. Sinder and J. Pelleg, Phys. Rev. E **60**, R6259 (1999).
[23] M. Sinder and J. Pelleg, Phys. Rev. E **61**, 4935 (2000).
[24] M. Sinder and J. Pelleg, Phys. Rev. E **62**, 3340 (2000).
[25] H. Taitelbaum *et al.*, Phys. Rev. Lett. **77**, 1640 (1996).
[26] B. Chopard *et al.*, Phys. Rev. E **56**, 5343 (1997).
[27] T. Unger and Z. Racz, Phys. Rev. E **61**, 3583 (2000).
[28] S.M. Cox and M.D. Finn, Phys. Rev. E **63**, 051102 (2001).
[29] M. Sinder and J. Pelleg, Phys. Rev. E **65**, 060101(R) (2002); M. Sinder, *ibid.* **65**, 037104 (2002).
[30] Note that at the chosen units of length, time, and concentration the reaction rate constant k is measured in units of $D/L^2 b_0$.