Diffusion-controlled death of $A$-particle and $B$-particle islands at propagation of the sharp annihilation front $A + B \to 0$

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We consider the problem of diffusion-controlled evolution of the system $A$-particle - $B$-particle island at propagation of the sharp annihilation front $A + B \to 0$. We show that this general problem, which includes as particular cases the sea-sea and the island-sea problems, demonstrates rich dynamical behavior from self-accelerating collapse of one of the islands to synchronous exponential relaxation of the both islands. We find a universal asymptotic regime of the sharp front propagation and reveal limits of its applicability for the cases of mean-field and fluctuation fronts.

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For the last decades the reaction-diffusion system $A + B \to 0$, where unlike species $A$ and $B$ diffuse and annihilate in a $d$-dimensional medium, has acquired the status of one of the most popular objects of research. This attractively simple system, depending on the initial conditions and on the interpretation of $A$ and $B$ (chemical reagents, quasiparticles, topological defects, etc.), provides a model for a broad spectrum of problems [1], [2]. A crucial feature of many such problems is the dynamical reaction front - a localized reaction zone which propagates between domains of unlike species.

The simplest model of a reaction front, introduced almost two decades ago by Galfi and Racz (GR) [3], is a quasi-one-dimensional model for two initially separated reactants which are uniformly distributed on the left side ($x < 0$) and on the right side ($x > 0$) of the initial boundary. Taking the reaction rate in the mean-field form $R(x,t) = k a(x,t) b(x,t)$, GR discovered that in the long-time limit $kt \to \infty$ the reaction profile $R(x,t)$ acquires the universal scaling form

$$ R = R_f \mathcal{Q} \left( \frac{x - x_f}{w} \right), \quad (1) $$

where $x_f \propto t_1^{1/2}$ denotes the position of the reaction front center, $R_f \propto t^{-3}$ is the height, and $w \propto t^2$ is the width of the reaction zone. Subsequently, it has been shown [4] - [8] that the mean field approximation can be adopted at $d \geq d_c = 2$, whereas in 1D systems fluctuations play the dominant role. Nevertheless, the scaling law (1) takes place at all dimensions with $\alpha = 1/6$ at $d \geq d_c = 2$ and $\alpha = 1/4$ at $d = 1$, so that at any $d$ the system demonstrates a remarkable property of the effective “dynamical repulsion” of $A$ and $B$: on the diffusion length scale $L_D \propto t_1^{1/2}$ the width of the reaction front asymptotically contracts unlimitedly: $w/L_D \to 0$ as $t \to \infty$. Based on this property a general concept of the front dynamics, the quasistatic approximation (QSA), has been developed [4] - [8], [9] which consists in the assumption that for sufficiently long times the kinetics of the front is governed by two characteristic time scales. One time scale $t_f = -(d \ln J/dt)^{-1}$ 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 that $t_f/t_f \ll 1$ from the QSA in the mean-field case with $D_{A,B} = D$ it follows [4], [5], [9]

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

whereas in the 1D case $w$ acquires the $k$-independent form $w \sim (D/J)^{1/2}$ [4], [5]. On the basis of the QSA a general description of spatiotemporal behavior of the system $A + B \to 0$ has been obtained for arbitrary nonzero diffusivities [10] which was then generalized to anomalous diffusion [11], diffusion in disordered systems [12], diffusion in systems with inhomogeneous initial conditions [13], and to several more complex reactions. Following the simplest GR model [3] the main attention has been traditionally 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, where asymptotically the stage of monotonous quasistatic front propagation is always reached: $t_f/t_f \to 0$ as $t \to \infty$.

Recently, in the work [14] a new line in the study of the $A + B \to 0$ dynamics has been developed under the assumption that the particle number of one of the species is finite, i.e., an $A$ particle island is surrounded by the uniform sea of particles $B$. It has been established that at sufficiently large initial number of $A$ particles $N_0$ and a sufficiently high reaction rate constant $k$ the death of the majority of island particles $N(t)$ proceeds in the universal scaling regime $N = N_0 \mathcal{G}(t/t_c)$, where $t_c \propto N_0^2$ is the lifetime of the island in the limit $k, N_0 \to \infty$. It has been shown that while dying, the island first expands to a certain maximal amplitude $x_f^M \propto N_0$ and then begins to contract by the law $x_f = x_f^M \frac{\zeta}{t_c} (t/t_c)$ so that on reaching $x_f^M$ (the turning point of the front)

$$ t_M/t_c = 1/e, \quad N_M/N_0 = 0.19886... \quad (3) $$

and, therefore, irrespective of the initial particle number and dimensionality of the system $\approx 4/5$ 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 this Rapid Communication we consider a much more general problem of the $A + B \to 0$ annihilation dynamics
with the initially separated reactants under the assumption that the particle number of the both species is finite. More precisely, we consider the problem on diffusion-controlled death of $A$-particle and $B$-particle islands at propagation of the sharp annihilation front $A + B → 0$.

We show that this island-island (II) problem, of which particular cases are the GR sea-sea (SS) problem and the island-sea (IS) problem \[14\], exhibits rich dynamical behavior and we reveal its most essential features.

Let in the interval $x ∈ [0, L]$ particles $A$ with concentration $a_0$ and particles $B$ with concentration $b_0$ be initially uniformly distributed in the islands $x ∈ [0, ℓ]$ and $x ∈ (ℓ, L]$, respectively. Particles $A$ and $B$ diffuse with diffusion constants $D_A$ and $D_B$ and when meeting they annihilate $A + B → 0$ with a reaction constant $k$. We will assume, as usually, that concentrations $a(x, t), b(x, t)$ change only in one direction (flat front) and we will consider that the boundaries $x = 0, L$ are impenetrable. Thus, our effectively one dimensional problem is reduced to the solution of the problem

$$\frac{\partial a}{\partial t} = D_A \nabla^2 a - R, \quad \frac{\partial b}{\partial t} = D_B \nabla^2 b - R \tag{4}$$

in the interval $x ∈ [0, L]$ at the initial conditions $a(x, 0) = a_0 \theta(ℓ - x), \ b(x, 0) = b_0 \theta(x - ℓ)$ and the boundary conditions $\nabla(a, b)|_{x=0, L} = 0$ where $\theta(x)$ is the Heaviside step function. To simplify the problem essentially we will assume $D_A = D_B = D$. 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 ratio of initial concentrations $a_0/b_0 = r$ and the ratio $ℓ/L = q$, we come from (4) to the simple diffusion equation for the difference concentration $s = a - b$

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

in the interval $x ∈ [0, 1]$ at the initial conditions

$$s_0(x ∈ [0, q)) = r, \quad s_0(x ∈ (q, 1]) = -1, \tag{6}$$

with the boundary conditions

$$\nabla s|_{x=0,1} = 0. \tag{7}$$

According to the QSA for large $k → ∞$ at times $t ∝ k^{-1} → 0$ there forms a sharp reaction front $w(x_f) → 0$ so that the solution $s(x, t)$ defines the law of its propagation $s(x_f, t) = 0$ and the evolution of particle distributions $a = s(x < x_f)$ and $b = |s|(x > x_f)$. In the limits sea-sea \[3\], $ℓ → ∞, L → ∞$ or island-sea \[14\] ($ℓ$ finite, $L → ∞$) the corresponding solutions $s_{SS}(x, t)$ and $s_{IS}(x, t)$ describe the initial stages of the system’s evolution at times $\sqrt{t} ≪ q, 1 - q$ and $q ≪ \sqrt{t} ≪ 1$, respectively. The general solution to Eqs. (5)-(7) for arbitrary $r, q$ and $t$ has the form

$$s(x, t) = \Delta + \sum_{n=1}^{∞} A_n(r, q) \cos(nπx)e^{-n^2π^2t}, \tag{8}$$

where coefficients $A_n(r, q) = (2(r + 1) \sin(nπq)/nπ$ and $\Delta(r, q) = N_A - N_B = rq - (1 - q)$ is the difference of the reduced number of $A$ and $B$ particles which remains constant. At $t > 1/π^2$ we find

$$s = \Delta + A_1(r, q) \cos(πx)e^{-π^2t} + \cdots. \tag{9}$$

Taking $s(x_f, t) = 0$ we obtain from (9) the law of the front motion

$$\cos(πx_f) = Ce^{π^2t} + \cdots, \tag{10}$$

where coefficient $C$ can be represented in the form

$$C = -Δ/A_1 = (q_⋆ - r)/A_1 = (q_⋆ - q)/q_⋆A_1, \tag{11}$$

where $q_⋆ = 1/(r + 1)$ and $r_⋆ = (1 - q)/q$ are the critical values of $q, r$ at which $C$ reverses its sign. From Eq. (10) it follows that at $|C| < 1/e$ and $r ≠ r_*, q ≠ q_*$, when the ratio of the initial particle numbers

$$\rho = \frac{N_{A_0}}{N_{B_0}} = \frac{r}{q_⋆} = \frac{(1 - q_⋆)q}{(1 - q)q_⋆} ≠ 1 \tag{12}$$

the front $x_f(t)$ moves either towards the boundary $x = 0$ $(ρ < 1)$ or towards the boundary $x = 1$ $(ρ > 1)$ so that in the limit $k → ∞$ the island of a smaller particle number $(A$ or $B$, respectively) dies within a finite time

$$t_c = (1/π^2) \ln |C|, \tag{13}$$

From Eqs. (10) and (13) we obtain

$$x_f = (1/π) \arccos(±e^{π^2(t - t_c)}), \tag{14}$$

(here and in what follows the upper sign corresponds to $ρ < 1$ and the lower sign corresponds to $ρ > 1$) whence for the front velocity $v_f = \dot{x}_f$ we find

$$v_f = -π \cot(πx_f) = π/\sqrt{e^{2π^2(t_c - t)} - 1}. \tag{15}$$

Making use then (13), for the distribution of particles $(a = s(x < x_f), b = |s|(x > x_f))$ at $ρ ≠ 1$ we obtain

$$s = \Delta(1 ± \cos(πx)e^{π^2(t_c - t)}) + \cdots. \tag{16}$$

Thus from the condition $N_A = \int_0^x sdx = N_B + Δ$ we find the laws of decay of the $A$ and $B$ particle number

$$N_A = (|Δ|/π)(\sqrt{e^{2π^2(t_c - t)} - 1} ± πx_f) \tag{17}$$

and then we derive finally the diffusive boundary current in the vicinity of the front

$$J = -∂s/∂x|_{x=x_f} = π|Δ|\sqrt{e^{2π^2(t_c - t)} - 1}, \tag{18}$$

which according to (2) defines evolution of the amplitude $R_f(t)$ and of the width of the front $w(t)$.

From Eqs. (13)-(18) we immediately come to the following important conclusions: for arbitrary $r$ and $q$ at $ρ < 1$ or $ρ > 1$ (i) the motion of the front is the universal function of the “distance” to the collapse time $t_c - t$ with
the remarkable property $x_f^>(t_c - t) = 1 - x_f^<(t_c - t)$. Moreover, the front velocity $v_f$ is the unique function of $x_f$ with the remarkable symmetry $x_f → 1 - x_f, v_f → -v_f$; (ii) the reduced particle number $N_A/|Δ|$ and the reduced boundary current $J/|Δ|$ are universal functions of $t_c - t$ with the remarkable properties $N_A^>(t_c - t) = N_A^<(t_c - t) - |Δ|$ and $J^>(t_c - t) = J^<(t_c - t)$.

Introducing the relative time $T = t_c - t$, from Eqs. (13)-(18) in the vicinity $T ≪ 1/π^2$ of the critical point $t_c$ we come to the universal power laws of self-accelerating collapse ($|v_f| ∝ T^{-1/2}$)

$$x_f^<, 1 - x_f^> = \sqrt{2T} + \cdots, \quad (19)$$

$$N_A^<, N_B^> = (\sqrt{8}/3)π^2 |Δ| |Δ|^{3/2} + \cdots, \quad (20)$$

$$J = \sqrt{2π} |Δ| \sqrt{T} + \cdots. \quad (21)$$

At large $t_c ≫ 1/π^2$ far from the critical point $T > 1/π^2$ according to Eqs. (13)-(18) there is realized the intermediate exponential relaxation regime ($|v_f| ∝ e^{-π^2T}$)

$$x_f^<, x_f^> = 1/2 ± e^{-π^2T}/π + \cdots, \quad (22)$$

$$N_A^<, N_B^> = (|Δ|/π)e^{π^2T}(1 ± πe^{-π^2T}/2 + \cdots), \quad (23)$$

$$J = π|Δ|e^{π^2T}(1 - e^{-2π^2T}/2 + \cdots), \quad (24)$$

which in the limit $t_c → (∎<C|q - 1| → 0)$ becomes dominant. Thus, at large $t_c ≫ 1/π^2$ the point $x_f ≈ 1/2$ (stationary front) is an "attractor" of trajectories. Exactly at the critical point $ρ_s = 1$ from Eqs. (9) and (10) we find $x_f^s = 1/2$ and obtain

$$N_s/N_0 = (2/π^2) \frac{\sin(πq)}{q(1 - q)} e^{-π^2s} + \cdots, \quad (25)$$

$$J_s = 2(\sin(πq)/q)e^{-π^2s} + \cdots. \quad (26)$$

In order to answer the question of when and how the "attractor" $x_f^s = 1/2$ is reached it is necessary to retain the next term ($n = 2$) in the sum (8). With allowance for the first two terms one can easily obtain

$$x_f^s = 1/2 - D(q)e^{-3π^2s} + \cdots \quad (27)$$

where $D(q) = (A_2/πA_1) = \sin(2πq)/2π\sin(πq)$. According to (27) at $q = 1/2$ the coefficient $D$ reverses its sign, therefore, as it is to be expected, at $q < 1/2$ and $q > 1/2$ the front reaches the attractor $x_f^s = 1/2$ from the left and the right, respectively. By combining (22) and (27), at small but finite $C$ we have $x_f^{<,>}$

$$1/2 - C e^{π^2s}/π - D e^{-3π^2s} + \cdots. \quad (28)$$

From this we conclude that under the condition $DC > 0$ there arises the turning point of the front $v_f^s = 0$ with the coordinates

$$t_M = (1/4π^2) \ln(λ_M |D/C|) + \cdots, \quad (28)$$

$$x_f^M = 1/2 - m_M D|C/D|^{3/4} + \cdots. \quad (29)$$

where $λ_M = 3π, m_M = 4/(3π)^{3/4}$, whereas at $DC < 0$ there arises the inflection point of the front trajectory $(|v_f^s| = \min |v_f|)$ with the coordinates $t_c, x_f^s$ which are determined by Eqs. (28), (29) with the coefficients $λ_s = 3λ_M, m_s = 2m_M/(3)^{3/4}$. The analysis presented demonstrates the key points of evolution of the island-island system at arbitrary $q$ and $r$ with $C(q,r) < 1/e$. Below we will focus on a detailed illustration of this evolution from the initial island-sea configuration ($q ≪ 1$).

A remarkable property of the island-sea configuration $q ≪ 1$ is that at $r ≫ 1$ the $Δ(ρ) = ρ - 1$ value and all the coefficients $A_n(ρ) = 2ρ$ up to $n = 1/q ≫ 1$ become unique functions of $ρ$. Therefore, the system’s evolution at $t ≫ q^2$ is determined by the sole parameter $ρ$. At $q^2 ≪ t ≪ 1$ we have the scaling IS regime

$$x_f = \sqrt{2t} ln^{1/2}(ρ^2/πt), \quad t_c(ρ) = ρ^2/π \quad (30)$$

with $x_f^M = ρ/2πtc, t_M = ρ^2/πe$. For $t > 1/4π^2$ with allowance for two principal modes ($n = 1, 2$) we obtain from (8)

$$x_f = (1/π) \arccos[G(ρ, t)e^{3π^2s}/4] \quad (31)$$

where $G(ρ, t) = \sqrt{1 + 8C(ρ)e^{-2π^2s} + 8e^{-6π^2s} - 1}$ and $C(ρ) = (1 - ρ)/2ρ$. For the time of collapse $t_c(ρ)$ we derive from (8) the general equation for arbitrary $ρ$

$$\sum_{n=1}^{∞} (±1)^n e^{-n^2π^2t_c(ρ)} = ±|C(ρ)| \quad (32)$$

whence for the leading terms in accord with (31) we find

$$t_c(ρ) = (|ln|C|| ± |C||^3 + \cdots)/π^2. \quad (33)$$

Using small $t$ representations of the series (32), one can easily show that, with the growing $ρ$, $t_c$ initially grows by the law $t_c(ρ) = ρ^2(1 + 4e^{-π^2/ρ^2} + \cdots)/π$, then it passes through the critical point $t_c(ρ_s) → ∞$ according to Eq.(33), and finally at large $ρ$ decays by the law $t_c(ρ) ∝ 1/ln ρ$. From Eqs. (31) and (17) for the starting points $t_{M,s}$ of front self-acceleration at small $C$ we find

$$t_{M,s}/t_c = 1/4 + β_{M,s}/|ln C| + \cdots \quad (34)$$

with the number of $A$ particles $N_A/M,s/N_A0 ∝ |C|^{1/4}$ where $β_M = β_s/2 = ln 3/4$. Remarkably, the same as for the scaling IS regime (3), (30) in the vicinity $|ρ - ρ_s| ≪ 1$ the ratio $t_M/t_c$ reaches the universal limit $t_M/t_c = 1/4$. In Fig. 1 are shown the calculated from (30) and
(31) trajectories of the front $x_f(t)$, which illustrate the evolution of the front motion with the growing $\rho$. It is seen that to $\rho \approx 0.7$ the death of the island $A$ proceeds in the scaling IS regime (30) ($t_M/t_c = 1/e$), then the $x_f(t)$ trajectory begins to deform, and at small $|\rho - \rho_*| \ll 1$ the regime of the dominant exponential relaxation (22)-(26). Substituting (26) into (2) for the exponential relaxation we find $\eta \sim e^{-(t-t_0)}$ where $\nu_{MF} = 1/3$ and $t_{Q}^{MF} = (\ln k)/\pi^2$. Substituting here $k \sim 10^{16}$ we obtain $t_{Q}^{MF} \sim 3.7$ and then from (25) we find $N_x^{MF}(\eta = 0.1)/N_0 \sim 10^{-13}$. The analogous calculation for the fluctuation 1D front gives $\nu_{F} = 3/4$, $T_{Q}^{F} \sim 1/(|\Delta|n_0)^{2/3}$ and $t_{Q}^{F} = 1/2$, $t_{Q}^{F} = (\ln n_0)/\pi^2$ where $n_0 = Lb_0$. Substituting here $n_0 \sim 10^6$ we find $T_{Q}^{F} \sim 10^{-4}/|\Delta|^{2/3}$, $t_{Q}^{F} \sim 1.4$ and $n_x^{F}(\eta = 0.1)/n_0 \sim 10^{-4}$. We conclude that both for the MF and the fluctuation fronts the vast majority of the particles die in the sharp front regime, therefore, the presented theory has a wide applicability scope.

In summary, the evolution of the system island $A$-island $B$ at the sharp annihilation front $A + B \rightarrow 0$ propagation has been first considered and a rich dynamical picture of its behavior has been revealed. The presented theory may have a broad spectrum of applications, e.g. in description of electron-hole luminescence in quantum wells [12], formation of nontrivial Liesegang patterns [16], and so on. Of special interest is the analogy of the island-island problem with the problem of annihilation on the catalytic surface of a restricted medium where for unequal species diffusivities in a recent series of papers [17] the phenomenon of annihilation catastrophe has been discovered. Study of the much more complicated case of unequal diffusivities and comparison with the annihilation dynamics on the catalytic surface is a generic and challenge problem for future.

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FIG. 1: (Color online) Evolution of the front trajectories $x_f(t)$ with growing $\rho$, calculated from Eqs. (30)(blue lines) and (31)(red circles) at $\rho = 0.5, 0.7, 0.9, 0.98, 1, 1.02, 1.1$ and $2$ (from left to right). The region of the scaling IS regime is shaded.
This figure "fig1.jpg" is available in "jpg" format from:

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