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LETTER TO THE EDITOR

Self-accelerating death of reacting species: sharp transition in long-time relaxation dynamics

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Abstract. Recently it has been discovered that an open system, where species A and B diffuse from the bulk of a restricted medium and die on its surface by the reaction $A + B \to 0$, exhibits a new type of kinetic transition: above some threshold difference in the initial numbers of particles, Δ_c, instead of the usual deceleration, the process of their death starts to accelerate autocatalytically. Here we study long-time relaxation dynamics of the system beyond the acceleration threshold and find it surprisingly rich. The main result is a *sharp transition* at the critical value Δ_r, above which the synchronism in relaxation of the species is destroyed and the asymptotics of their death loses its universality.

In the last few decades, studies of nonlinear reaction–diffusion (RD) systems have been developed into one of the most popular and fascinating fields of nonlinear dynamics. The scope of such systems involves different branches of physics, chemistry and biology, and extends from complex autocatalytic systems, displaying spontaneous formation of Turing structures and chemical turbulence, to most simple ones with the bimolecular reaction $A + B \to 0$ displaying dynamical clustering [1]. So far, however, the main attention has focused on RD systems, in which both reaction and diffusion proceed in the *bulk of the extended medium*. In contrast, we have recently demonstrated that in another wide class of RD systems, where reaction and diffusion are *spatially separated*; the interplay between reaction and diffusion acquires qualitatively new features and leads to new dynamics of the bimolecular reaction $A + B \to 0$, which is the most abundant one in nature [2]. Namely, we have found that once particles A and B diffuse at different mobilities from the bulk of the restricted medium onto the surface and die on it by the reaction $A + B \to 0$, there should exist some threshold difference in the initial numbers of A and B particles, Δ_c, above which the process of their death, instead of the usual deceleration for biomolecular reactions, starts to *accelerate autocatalytically*.

The deceleration–acceleration transition has been shown to arise as a result of competition in the slow species diffusion–reaction chain, which leads to 'switching on' of the loop of positive feedback above the threshold level Δ_c, and this can be interpreted as a *new type of self-organization* in open nonlinear systems. However, while the adiabatic approximation developed allows one to understand clearly the mechanism of the transition and to calculate exactly the critical transition point Δ_c, the following important questions remain open: How does the relaxation dynamics change with growth of Δ beyond the acceleration threshold, where the adiabatic approximation loses its applicability? How does such an evolution depend on the ratio of species diffusivities? What is the role of the initial

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conditions? In this letter we answer these questions in the long-time asymptotic limit and report on a new kinetic transition at some critical value Δ_r, above which the synchronism in relaxation of the species is destroyed and the asymptotics of their death loses its universality.

We consider a model in which species A and B are supposed to be initially uniformly distributed in the bulk of an infinitely extended slab of thickness 2ℓ. Both species diffuse to the surface ($X = \pm\ell$) and desorb as a result of the surface reaction $A_{ads} + B_{ads} \to AB$. The rate of the reaction is proportional to the product of surface concentrations $I = kn_An_B = \kappa N_{As}N_{Bs}$, where the rates of surface–subsurface exchange are supposed to be rather high, so that quasi-equilibrium $n_i = f_iN_{is}$ between concentrations on the surface and in the subsurface layer is always sustained. Because of planar spatial homogeneity the system is effectively one-dimensional and the boundary conditions for diffusion equations can be found from the equality of diffusion I^D and desorption I flux densities at the surface $I^D|_s = I$†. Then introducing the index 'H' (*heavy*) for the slower diffusing species and the index 'L' (*light*) for the faster one the boundary value diffusion problem of species evolution reads [2] (by symmetry we consider the interval $[0, \ell]$ only)

$$\partial C_H/\partial\tau = \nabla^2 C_H \qquad \partial C_L/\partial\tau = (1/p)\nabla^2 C_L \tag{1a}$$

$$\nabla C_H|_s = (1/p)\nabla C_L|_s = -C_{Hs}C_{Ls} \tag{1b}$$

with $\nabla C_i|_{x=0} = 0$ and the initial conditions $C_i(x, \tau = 0) = C_i(0)$. Here $\nabla \equiv \partial/\partial x$, $x = X/\ell \in [0, 1]$ is the non-dimensional coordinate, $\tau = D_Ht/\ell^2$ is the non-dimensional time, $p = D_H/D_L \leqslant 1$ is the ratio of species diffusivities, $C_i(x, \tau) = N_i/N_*$ are the reduced concentrations, and $N_* = D_H/\kappa\ell$ is the characteristic concentration scale, from which diffusion starts to play an essential role. Boundary conditions (1b) reflect the fact that particles disappear in pairs only and, therefore, the difference in the numbers of H and L particles remains constant

$$\langle C_H\rangle - \langle C_L\rangle = \Delta = \text{constant}$$

i.e. the excess amount stays 'inert' in the bulk (here $\langle C_i\rangle = \int_0^1 C_i\,\mathrm{d}x = \mathcal{N}_i/\mathcal{N}_*$ are the total reduced numbers of particles per unit of slab surface and $\mathcal{N}_* = D_H/\kappa$ is the characteristic scale of the number of particles). This 'inert' part of the majority species $\Delta = \delta\mathcal{N}/\mathcal{N}_*$ acts as a control parameter, whereas its 'active' (capable of desorbing) part $\mathbf{N} = \mathcal{N}_{pair}/\mathcal{N}_*$, which equals the total number of H–L pairs, acts as the only variable.

Reference [2] focused on the main characteristics of relaxation dynamics—the lifetime of the pairs

$$\tau_{pair}^{-1} = -\mathrm{d}\ln\mathbf{N}/\mathrm{d}\tau$$

in the case $\Delta > 0$, when heavy particles are in excess. Here the number of pairs is determined by the number of L particles, $\mathbf{N} = \langle C_L\rangle$, so the dynamics of their death depends crucially on the behaviour of the surface concentration of H particles, C_{Hs}. In the limit of $p \to 0$, when the distribution of L particles in the bulk remains uniform due to their fast diffusion and the lifetime $\tau_{pair}^{-1} = C_{Hs}$, the key results of [2] may be formulated as follows.

(i) When parameter Δ, playing effectively the role of the Rayleigh number, achieves the threshold value $\Delta_c = \omega_0 = \pi^2/4$ (ω_0 is the main eigenfrequency of the diffusion field

† A strict condition of balance of fluxes has the form $J_i^D|_s = J + d_i\dot{C}_{is}$, where the parameter $d_i = f_i/\ell$ shows the relative capacity of the surface layer [2]. Therefore, equality of fluxes $J_i^D|_s = J$ takes place within the limit $d_i \to 0$, when the surface layer capacity can be neglected. At comparatively high temperatures the surface segregation coefficient is evaluated usually as $f \sim (1\text{–}10^2)a$, where a is the lattice parameter and thus, for samples of macroscopic size, such an approximation due to the smallness of the parameter d is as a rule fulfilled with good reserve.

relaxation under absorbing boundary conditions), the system undergoes a kinetic transition from the *deceleration phase* ($C_{Hs}\downarrow$) to the state where the surface concentration of H particles and, therefore the rate of death, only increase with time $C_{Hs}\uparrow$ (*acceleration phase*).

(ii) If $\dot{C}_{Hs}$ does not change too fast $|\zeta| = |\ddot{C}_{Hs}/\dot{C}_{Hs}| \lesssim \omega_0$ (adiabatic approximation) the system after a short transient stage goes onto the universal trajectory

$$\dot{C}_{Hs} = (\Delta - \omega_0)\alpha_0(\mathbf{N})(1 - \eta(\mathbf{N})) \tag{2}$$

($\alpha_0 = \omega_0^2\mathbf{N}(\mathbf{N} + \Delta)/(\mathbf{N} + \omega_0)^3$ and $\eta \ll 1$), along which, starting from $\mathbf{N} \to \infty$, the rate $\dot{C}_{Hs}$ beyond the threshold grows together with C_{Hs} (the growth of C_{Hs} accelerates the drop of $\mathbf{N} \to$ the drop of $\mathbf{N}$ accelerates the growth of C_{Hs} and so on), i.e. the process of death develops *autocatalytically* (*phenomenon of self-accelerating death*), and then reaching a maximum at $\mathbf{N} \sim 1$, it decreases infinitely, being positive up to $\mathbf{N} \to 0$. According to (2), asymptotically far beyond the transition point the adiabaticity condition is violated rapidly ($|\zeta||_{\tau\to\infty} \sim \Delta$); therefore, applicability of (2) is limited by the values of $\Delta/\Delta_c \sim 1$.

In this letter we present an approach free from this restriction. More specifically, we derive exact expressions for leading spatial modes, which describe the long-time relaxation dynamics of the system at arbitrary values of Δ, and the ratio of species diffusivities p.

We start from the fact that, in the limit $\tau \to \infty$, $C_{Hs} \to \Delta$ and therefore the dominating term in the light species decay asymptotics is $C_L(x, \tau) = \mathcal{L}_1 \cos(qx)\, e^{-\omega\tau}$, where the wavenumber $q = \sqrt{p\omega}$ and the relaxation frequency ω of the leading mode is determined as the least positive root of the equation [3]

$$\Delta = \sqrt{\omega/p}\tan(\sqrt{p\omega}). \tag{3}$$

Assuming $\mathcal{L}_1 = \sqrt{p\omega}/\sin(\sqrt{p\omega})$ ($\mathcal{L}_1 = 1$ at $p \to 0$), that is, shifting for convenience the origin of time so that $\langle C_L\rangle|_{\tau\to\infty} = e^{-\omega\tau}$, we find as $\tau \to \infty$ the problem for $C_H(x, \tau)$ with the boundary condition

$$\nabla C_H|_s = -\omega\, e^{-\omega\tau}. \tag{4}$$

The solution of (1*a*) and (4) at $\omega \neq \pi^2 n^2$ ($n = 1, 2, \ldots$) has the form

$$C_H = \Delta + \mathcal{H}_1 \cos(\sqrt{\omega}x)\, e^{-\omega\tau} + S \tag{5}$$

where $\mathcal{H}_1 = \sqrt{\omega}/\sin(\sqrt{\omega})$, and the sum $S = \sum_{n=1}^{\infty} \mathcal{S}_n \cos(n\pi x)\, e^{-n^2\pi^2\tau}$ describes the eigenmodes of the diffusion field relaxation under neutral (non-flux) boundary conditions ($\nabla S|_s = \langle S\rangle = 0$). According to (5) the H-field asymptotics consist of the terms generated by the reaction and of those associated with the relaxation of the distribution of 'pairless' H particles, which carry information on the prehistory of the system. At $\omega = \omega_n = \pi^2 n^2$ the reaction excites a 'resonance' in the corresponding S-mode ($\mathcal{H}_1 \to \infty$) and the solution acquires the form

$$C_H^r = \Delta + \mathcal{R}_n(\tau\cos(n\pi x) + (1/2\pi n)x\sin(n\pi x))\, e^{-n^2\pi^2\tau} + S \tag{6}$$

where $\mathcal{R}_n = (-1)^{n+1}2\pi^2 n^2$. The following important results immediately follow from equation (5).

(i) Equation (5) reproduces rigorously a conclusion on the existence of a deceleration–acceleration kinetic transition for an *arbitrary* $p < 1$ at the threshold value

$$\Delta_c = (\pi/2\sqrt{p})\tan(\pi\sqrt{p}/2).$$

Indeed, according to (5) $\delta C_{Hs}|_{\tau\to\infty} = C_{Hs} - \Delta = -\omega^{-1}\dot{C}_{Hs} = \mathcal{H}_{1s}\, e^{-\omega\tau}$, where $\mathcal{H}_{1s} = \sqrt{\omega}\cot\sqrt{\omega}$ at the critical point $\omega_c = \omega_0 = \pi^2/4$ changes sign ($C_{Hs}\downarrow \to C_{Hs}\uparrow$), which results in acceleration of the death of pairs (see below).

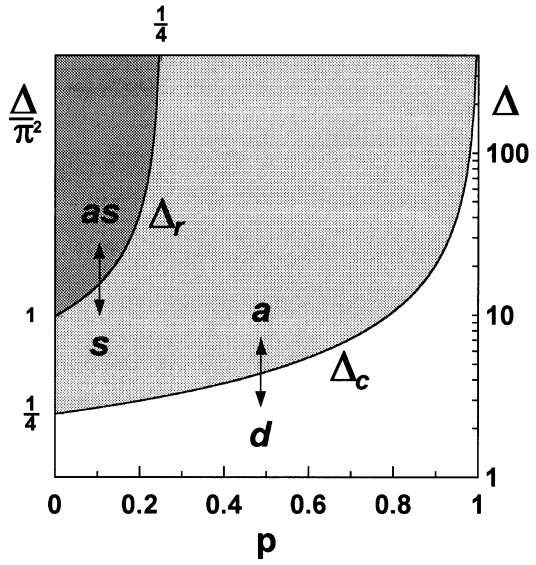

Figure 1. Δ–p diagram of deceleration–acceleration and synchronous relaxation–asynchronous relaxation kinetic transitions.

(ii) Equation (5) provides the key result of the present paper, which reads that, due to competition between the main 'reaction' mode $\mathcal{H}_1 \cos(\sqrt{\omega}x)\,\mathrm{e}^{-\omega\tau}$ and the main 'non-flux' mode $\mathcal{S}_1 \cos(\pi x)\,\mathrm{e}^{-\pi^2\tau}$ with Δ growing beyond the acceleration threshold Δ_c, the system undergoes a *new kinetic transition* from the state in which the *'reaction driven'* relaxation dominates asymptotically to that in which *'non-flux'* or *'internal'* relaxation of the H-field dominates: $\mathcal{H}_1 \cos(\sqrt{\omega}x)\,\mathrm{e}^{-\omega\tau} \to \mathcal{S}_1 \cos(\pi x)\,\mathrm{e}^{-\pi^2\tau}$. This transition takes place at the critical value $\omega_\mathrm{r} = \pi^2$, i.e. at the critical number of 'pairless' particles

$$\Delta_\mathrm{r} = (\pi/\sqrt{p})\tan(\pi\sqrt{p}).$$

According to (3) $\omega_{\max} = \omega|_{\Delta\to\infty} = \pi^2/4p$, so the transition point can be achieved only if the ratio of diffusivities is less than the critical value $p_\mathrm{r} = 1/4$ (figure 1).

To clarify the main features of the transition we write, according to (5), $J = C_{Hs}C_{Ls} = \omega\,\mathrm{e}^{-\omega\tau} + \mathcal{J}_2\,\mathrm{e}^{-2\omega\tau} + \mathcal{J}_*\,\mathrm{e}^{-(\pi^2+\omega)\tau} + \cdots$ with unknown coefficients $\mathcal{J}_2$ and $\mathcal{J}_*$. Apparently, each term in the asymptotics J operates as an additive 'sink' of the power $\mathcal{J}'\,\mathrm{e}^{-\omega'\tau}$, which should generate a diffusive response of the form $\mathcal{L}'\cos(\sqrt{p\omega'}x)\,\mathrm{e}^{-\omega'\tau}$ for L species and of the form $\mathcal{H}'\cos(\sqrt{\omega'}x)\,\mathrm{e}^{-\omega'\tau}$ for H species. Extending this procedure and equalling the coefficients at similar exponents in (1*b*), it is easy to determine the sequence of the first two leading modes in L and H asymptotics and, therefore, to obtain the asymptotics of τ_pair^{-1}. Below the transition point $\omega < \pi^2(\Delta < \Delta_\mathrm{r})$ we find

$$C_L = \mathcal{L}_1 \cos(\sqrt{p\omega}x)\,\mathrm{e}^{-\omega\tau} + \mathcal{L}_2 \cos(\sqrt{2p\omega}x)\,\mathrm{e}^{-2\omega\tau} \tag{7a}$$

$$C_H = \Delta + \mathcal{H}_1 \cos(\sqrt{\omega}x)\,\mathrm{e}^{-\omega\tau} + \begin{cases} \mathcal{H}_2 \cos(\sqrt{2\omega}x)\,\mathrm{e}^{-2\omega\tau} \\ \mathcal{S}_1 \cos(\pi x)\,\mathrm{e}^{-\pi^2\tau} \end{cases} \tag{7b}$$

$$\tau_\mathrm{pair}^{-1} = \omega + \mathcal{P}\,\mathrm{e}^{-\omega\tau} + \cdots \tag{7c}$$

where $\mathcal{L}_2 = p\omega\mathcal{H}_{1s}/Q(\sqrt{2p\omega})\Delta$, $Q(z) = z\sin z - p\Delta\cos z$, $\mathcal{H}_2 = \mathcal{L}_2\sin(\sqrt{2p\omega})/\sqrt{p}\sin(\sqrt{2\omega})$ and $\mathcal{P} = \mathcal{L}_2\sin(\sqrt{2p\omega})\sqrt{\omega/2p}$.

Beyond the transition point $\omega > \pi^2 (\Delta > \Delta_r)$ we find

$$C_L = \mathcal{L}_1 \cos(\sqrt{p\omega}x)\, e^{-\omega\tau} + \mathcal{S}_* \cos(\sqrt{p\omega_*}x)\, e^{-\omega_*\tau} \tag{8a}$$

$$C_H = \Delta + \mathcal{S}_1 \cos(\pi x)\, e^{-\pi^2\tau} + \begin{cases} \mathcal{H}_1 \cos(\sqrt{\omega}x)\, e^{-\omega\tau} \\ \mathcal{S}_2 \cos(2\pi x)\, e^{-4\pi^2\tau} \end{cases} \tag{8b}$$

$$\tau_{pair}^{-1} = \omega + \mathcal{P}_* e^{-\pi^2\tau} + \cdots \tag{8c}$$

where $\mathcal{S}_* = -p\omega\mathcal{S}_1/Q(\sqrt{p\omega_*})\Delta$, $\mathcal{P}_* = \pi^2\mathcal{S}_* \sin(\sqrt{p\omega_*})/\sqrt{p\omega_*}$ and $\omega_* = \omega + \pi^2$.

We see that in the 'reaction' phase (7) both L and H fields asymptotically relax synchroneuosly as $\sim e^{-\omega\tau}$ and go into a universal distribution at which $\delta C_{Hs}|_{\mathbf{N}\to 0} = \mathcal{H}_{1s}\mathbf{N}$ and $\delta\tau_{pair}^{-1}|_{\mathbf{N}\to 0} = \mathcal{P}\mathbf{N}$ depend only on the current number of pairs $\mathbf{N}$ at an *arbitrary initial distribution* of species. At the critical point Δ_c, both $\mathcal{P}$ and $\mathcal{H}_{1s}$ change sign $(+ \to -)$, i.e. at any p the $C_{Hs}\downarrow \to C_{Hs}\uparrow$ transition 'switches' the system over to the acceleration state: $\tau_{pair}^{-1}\downarrow \to \tau_{pair}^{-1}\uparrow$. It is essential that exactly at the critical point Δ_c, where an adiabatic approximation is inapplicable, it follows from (7*b*) that $\delta C_{Hs}^c|_{\tau\to\infty,\mathbf{N}\to 0} = -\mathcal{S}_1 e^{-\pi^2\tau} = -\mathcal{S}_1\mathbf{N}^4$. Correspondingly, due to $\mathcal{L}_2^c = \mathcal{H}_2^c = \mathcal{H}_{1s}^c = 0$ from (8*c*) instead of (7*c*), it follows that $(\delta\tau_{pair}^{-1})_c|_{\tau\to\infty,\mathbf{N}\to 0} = \mathcal{P}_*^c(\mathcal{S}_1)\, e^{-\pi^2\tau} = \mathcal{P}_*^c(\mathcal{S}_1)\mathbf{N}^4$. Hence, exactly at the critical point Δ_c relaxation of δC_{Hs} and $\delta\tau_{pair}^{-1}$ proceeds much faster than before and after one

$$\mathbf{N} \to (\mathbf{N}^4)_c \to \mathbf{N} \tag{9}$$

and in the general case the critical relaxation trajectory depends on the prehistory of the system. Beyond the transition point $\Delta > \Delta_r$, relaxation of the H field becomes autonomously $\sim e^{-\pi^2\tau}$, that is the synhchronism of H and L relaxation *is destroyed*. The second important consequence of the transition is that the asymptotic law of the $\delta C_{Hs}|_{\mathbf{N}\to 0} = -\mathcal{S}_1\mathbf{N}^{\pi^2/\omega}$ and $\delta\tau_{pair}^{-1}|_{\mathbf{N}\to 0} = \mathcal{P}_*(\mathcal{S}_1)\mathbf{N}^{\pi^2/\omega}$ decay *loses its universality* because in the general case $\mathcal{S}_1$ depends on the initial number of pairs $\mathbf{N}_0$ and on the initial distribution of species. Exactly at the Δ_r point, according to (6), the main non-flux mode is excited 'resonantly' and we have $C_H^r = \Delta_r + 2\pi^2 \cos(\pi x)\tau\, e^{-\pi^2\tau} + \cdots$. Therefore, $\delta C_{Hs}^r|_{\tau\to\infty,\mathbf{N}\to 0} = -2\pi^2\tau\, e^{-\pi^2\tau} = 2\mathbf{N}\ln\mathbf{N}$ and, correspondingly, $(\delta\tau_{pair}^{-1})_r|_{\tau\to\infty,\mathbf{N}\to 0} = -\pi^2\mathcal{P}_*^r\tau\, e^{-\pi^2\tau} = \mathcal{P}_*^r\mathbf{N}\ln\mathbf{N}$ with $\mathcal{P}_*^r = \pi^3\sqrt{2p}\sin(\pi\sqrt{2p})/Q(\pi\sqrt{2p})\Delta_r$.

Summarizing, we conclude that at $p < p_r = 1/4$ the dynamical state with the death of pairs accelerating along a universal asymptotic trajectory exists only up to a 'resonant' transition line $\Delta_r(p)$, above which both the trajectory and character (acceleration or deceleration) of the relaxation dynamics in the general case become dependent on the initial distribution of the species and, in our case of a uniform initial distribution, on the initial pair number $\mathbf{N}_0$ ($\mathcal{H}_1(\Delta, p) \to \mathcal{S}_1(\Delta, p, \mathbf{N}_0)$). In this new 'phase', the relaxation rates $\tau_{Hs}^{-1} = -\mathrm{d}\ln|\delta C_{Hs}|/\mathrm{d}\tau|_{\tau\to\infty}$ and $\Omega = -\mathrm{d}\ln|\delta\tau_{pair}^{-1}|/\mathrm{d}\tau|_{\tau\to\infty}$ do not change with increasing Δ,

$$\Omega = \tau_{Hs}^{-1} = \begin{cases} \omega & \Delta_c < \Delta \leqslant \Delta_r \\ \pi^2 & \Delta > \Delta_r \end{cases} \tag{10}$$

i.e. while crossing the Δ_r line the derivative $\mathrm{d}\Omega/\mathrm{d}\Delta$ varies in jumps down to zero and the asymptotic law of the δC_{Hs} and $\delta\tau_{pair}^{-1}$ decay changes as follows:

$$\mathbf{N} \to (\mathbf{N}\ln\mathbf{N})_r \to \mathbf{N}^{\pi^2/\omega}. \tag{11}$$

The imperative question arises now of what is the sign of the amplitude $\mathcal{S}_1$ and how does $\mathcal{S}_1$ depend on the initial pair number $\mathbf{N}_0$. We begin with the case $\mathbf{N}_0 \to 0$ and for

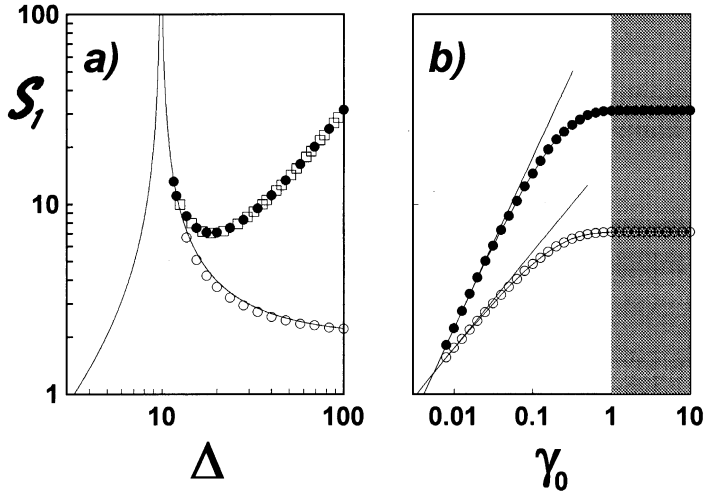

Figure 2. (*a*) $\mathcal{S}_1$ as a function of Δ, calculated numerically at $\mathbf{N}_0 = 1$ (open circles), $\gamma_0 = 1$ (full circles) and $\gamma_0 = 10$ (squares) for $p = 0$. The curve stands for the dependence $2/|\sigma|, \sigma = 1 - \pi^2/\Delta$; (*b*) $\mathcal{S}_1$ as a function of γ_0, calculated numerically at $\Delta = 20$ (open circles) and $\Delta = 10^2$ (full circles) for $p = 0$. The lines show the dependences $\mathcal{S}_1(\gamma_0)$ calculated by (12).

simplicity consider the $p \to 0$ limit. In this case, neglecting the terms $\mathcal{O}(\mathbf{N}_0^2)$, we write $C_L = \mathbf{N} = \mathbf{N}_0\,\mathrm{e}^{-\Delta\tau}$ and therefore for $\Delta \neq \pi^2 n^2$ we get

$$C_H = \Delta + \frac{\mathbf{N}_0\sqrt{\Delta}}{\sin\sqrt{\Delta}}\cos(\sqrt{\Delta}x)\,\mathrm{e}^{-\Delta\tau} + \sum_1^\infty \tilde{\mathcal{S}}_n \cos(n\pi x)\,\mathrm{e}^{-n^2\pi^2\tau}.$$

Under a uniform initial distribution this immediately yields $\tilde{\mathcal{S}}_n = (-1)^{n+1}2\mathbf{N}_0\Delta/(\Delta - \pi^2 n^2)$ and, after returning to the shifted time $(\Delta\tau)|_{\mathbf{N}\to 0} = -\ln\mathbf{N}$, we find

$$\mathcal{S}_1 = 2\mathbf{N}_0^\sigma/\sigma \qquad \sigma = 1 - \pi^2/\Delta. \tag{12}$$

According to (12), at the Δ_r point the amplitude $\mathcal{S}_1$ changes sign ($- \to +$), i.e. above the Δ_r transition $\mathcal{S}_1 > 0$. This means that as $\mathbf{N}_0 \to 0$ above the Δ_c threshold, the death of pairs always accelerates, whereas at the critical point $\mathcal{S}_1^\mathrm{c} = -(2/3)\mathbf{N}_0^{-3}$ the death of pairs is decelerated in time. It would be natural to expect that under a uniform initial distribution the diffusive flux in the bulk should always be directed towards the surface, and therefore above Δ_r we must have $\mathcal{S}_1 > 0$ at any values of $\mathbf{N}_0$. We have studied numerically the dependence $\mathcal{S}_1(\mathbf{N}_0)$ at $\Delta > \Delta_\mathrm{r}$ and it was a surprise to find that, starting from $\gamma_0 = \mathbf{N}_0/\Delta = \gamma_0^\mathrm{u} \simeq 1$, when the initial number of pairs becomes equal to that of 'pairless' particles, the amplitude $\mathcal{S}_1$ stops (with an exponential accuracy) being dependent on the initial number of pairs (figure 2)

$$\mathcal{S}_1 = 2f^\sigma/\sigma \qquad f|_{\gamma_0 \geqslant 1} = f^\mathrm{u}(\Delta)(1 - \mathcal{O}(\mathrm{e}^{-\alpha\gamma_0})) \tag{13}$$

that is, the system goes onto a universal asymptotic trajectory, along which the rate of death of pairs depends on their current number $\mathbf{N}$ only. The global picture of 'universalization' is illustrated by figure 3, which depicts the phase portrait of the evolution of the trajectory $\dot{C}_{Hs} = \varphi(\mathbf{N})$ with an increasing initial number of pairs. Figure 3(*b*) shows that an increase

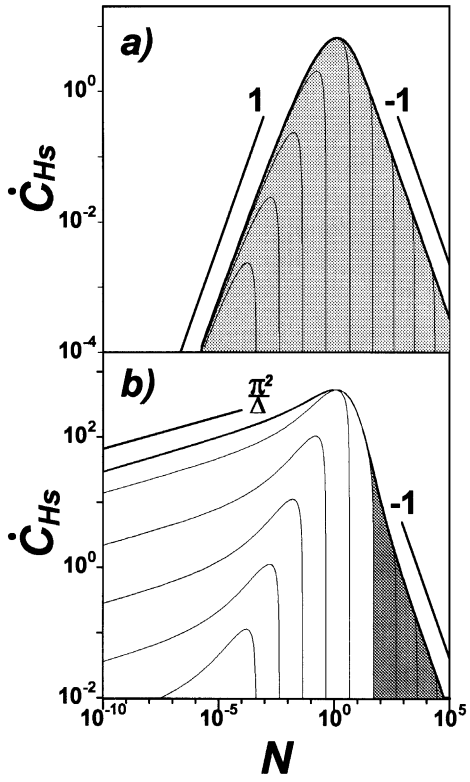

Figure 3. Trajectories of $\dot{C}_{\rm Hs} = \varphi(\mathbf{N})$, calculated numerically at $\mathbf{N}_0 = 10^{-3}$, 10^{-2}, 10^{-1}, 1, 10, 10^2, 10^3, 10^4, 10^5 (from left to right) and 10^8 (bold line) at $p = 0$ for (*a*) $\Delta = 8 < \Delta_{\rm r}$ and (*b*) $\Delta = 10^2 > \Delta_{\rm r}$. The region of trajectories outgoing onto the universal asymptotics is darkened (initial transient sections with $\dot{C}_{Hs} < 0$ are not shown).

of $\mathbf{N}_0$ within the weak nonlinearity regime ($\gamma_0 \ll 1$) leads to a self-similar shift of the trajectory in accordance with the scaling

$$\dot{C}_{Hs} = \mathbf{N}_0 \mathcal{G}(\mathbf{N}/\mathbf{N}_0)$$

($\mathrm{Max}\,\dot{C}_{Hs} \propto \mathbf{N}_0, \mathbf{N}_{\max} \propto \mathbf{N}_0$) resulting from the expression for C_H. This continues until strong nonlinearity comes into play and finally, when the threshold $\gamma_0^{\rm u} \simeq 1$ is achieved, not only the asymptotics, but also all the decaying 'branch' of the trajectory together with $\mathrm{Max}\,\dot{C}_{Hs}$ become universal 'simultaneously'. Thus at $\gamma_0 > \gamma_0^{\rm u} \simeq 1$ the reaction '*erases*' the information on the initial distribution and creates its *own* distribution which predetermines universality of long-time asymptotics. Further growth in γ_0 up to $\gamma_0 \to \infty$ results in progressing 'universalization' of the trajectory's autocatalytic 'branch', until a single universal trajectory $\dot{C}_{Hs}^{\rm u}$ is formed (figure 3, bold curve). Note that far from the maximum ($\mathbf{N}/\Delta \gg 1$) an increase in $\dot{C}_{Hs}^{\rm u}$ on the autocatalytic 'branch' of this trajectory in accordance with (2) obeys the law $\dot{C}_{Hs}^{\rm u} = (\Delta - \Delta_{\rm c})\omega_0^2/\mathbf{N} \propto \mathbf{N}^{-1}$, which is indicated in figure 3 by the line with slope -1 (within the limit $\gamma_0 \to \infty$ at $\mathbf{N}/\Delta \to \infty$ the adiabatic approximation [2] remains correct at any Δ). The numerical calculations, which will be presented in detail elsewhere [4], show that such a pattern takes place within the whole range of $0 < p < 1/4$, but with increasing p the value of $\gamma_0^{\rm u}(p)$ is displaced to $\gamma_0^{\rm u} > 1$. Moreover, within the $\Delta \to \infty$ limit the behaviour of $\dot{C}_{Hs}^{\rm u}$ beyond the maximum ($\mathbf{N} < \mathbf{N}_{\max}$)

can be described by the scaling function

$$\dot{C}^{\mathrm{u}}_{Hs} = \Delta\mathcal{F}(\mathbf{N}/\Delta)$$

whence, taking account of $\dot{C}_{Hs}|_{\mathbf{N}\to 0} \propto \mathbf{N}^{4p}$ (11), it follows that $\mathcal{S}^{\mathrm{u}}_1|_{\Delta\to\infty} \propto \Delta^{1-4p}$.

In conclusion, in this letter a complete picture of long-time relaxation dynamics in the catalytic reaction–diffusion system $A + B \to 0$ at arbitrary values of the number of pairless particles Δ, ratio of species diffusivities p and initial number of pairs $\mathbf{N}_0$ has been described. We have shown that, beyond the acceleration threshold, a sharp kinetic transition from *universal synhronous relaxation to non-universal asynchronous relaxation* arises ($p < p_{\mathrm{r}}$, $\Delta > \Delta_{\mathrm{r}}$) and we have demonstrated numerically that there exists a typical ratio of the initial number of pairs to that of pairless particles, γ^{u}_0, above which the long-time asymptotics of the death of pairs becomes universal surprisingly abruptly. An exceptionally interesting question has been left beyond the scope of our analysis. It is the question on the character of variation of the death of pairs dynamic at the point of transition from the autocatalytic stage to the stage of decaying growth of C^{u}_{Hs} (figure 3), which requires separate consideration. Our preliminary results show that in the 'thermodynamic limit', $\Delta \to \infty$, at this point the relaxation rate of desorption flux $\tau_J^{-1} = -\mathrm{d}\ln J/\mathrm{d}\tau$ increases *discontinuously*, i.e. a discontinuous transition in time arises in the system ('*flux breaking effect*'), which has no analogue in the literature. A detailed discussion of this transition is expected to be presented in a future report.

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