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Formation of a finite-time singularity in diffusion-controlled annihilation dynamics

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Abstract

I review the basic features of formation of the universal annihilation catastrophe which develops in an open system, where species A and B diffuse from the bulk of a restricted medium and die on its surface (desorb) by the reaction $A + B \rightarrow 0$. This phenomenon arises in the diffusion-controlled limit as a result of self-organizing explosive growth (drop) of the surface concentrations of, respectively, slow and fast particles (concentration explosion) and manifests itself in the form of an abrupt singular jump of the desorption flux relaxation rate. I present a systematic scaling theory of passage through the point of singularity and demonstrate the results of extensive numerical calculations illustrating its main features. In conclusion I discuss the conditions and possibilities of an experimental observation of the annihilation catastrophe and point out some prospective lines for its generalization.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Finite-time singularities—blow-up solutions developing from smooth initial conditions at a particular time—provide probably the most dramatic manifestation of strongly nonlinear effects that can occur in nature [1]. The formation of finite-time singularities is observable in a broad spectrum of nonlinear systems (Jang–Mills fields [2], black holes [3], self-gravitating Brownian particles [4], turbulent flows [5], jet eruption [6] and earthquakes [7] to name only a few) and so the description of scenarios of the development of finite-time singularities is a fundamental problem which attracts wide interdisciplinary interest. The aim of this review paper is to give an insight into the scaling theory of annihilation catastrophe which is the first finite-time singularity phenomenon arising in the purely 'sink' reaction–diffusion system $A + B \rightarrow 0$.

The irreversible bimolecular reaction between unlike diffusing species $A + B \rightarrow 0$ is one of the most abundant reactions, depending on the interpretation of A and B (chemical reagents, quasiparticles, topological defects, etc), playing the key role in a broad spectrum of problems. After the pioneering works by Ovchinnikov and Zeldovich [8] and Toussaint and Wilczek [9] (*spontaneous growth of single species domains*) and by Galfi and Racz [10] (*propagation of localized reaction front*) interest in the reaction–diffusion system $A + B \to 0$ increased significantly and for the last decades this system has acquired the status of one of the most popular objects of research (for a review see [11–15] and references therein). The majority of papers in this field are traditionally devoted to systems where both reaction and diffusion proceed in the bulk of a d-dimensional medium.

Here I focus on another wide class of systems where reaction proceeds on the *catalytic surface* of a medium whereas diffusion proceeds in its bulk. In the work [16] it was first demonstrated that in this class of systems the interplay between reaction and diffusion acquires qualitatively new features and leads to a new type of self-organization. It has been found that once particles A and B diffuse at different mobilities from the bulk of a restricted medium onto the surface and die on it (desorb) by the reaction $A + B \to 0$, there exists some threshold difference in the initial numbers of A and B particles, Δ_c, above which *the loop of positive feedback* is 'switched on' and the process of their death, instead of the usual deceleration, starts *to accelerate autocatalytically* [16, 17]. Recently, it has been discovered [18] that the deceleration–acceleration transition is a prelude to much more nontrivial dynamical effects: in the diffusion-controlled limit $\Delta \to \infty$ a new critical phenomenon develops—*annihilation catastrophe*—which arises as a result of self-organizing explosive growth (drop) of the surface concentrations of, respectively, slow and fast particles (*concentration explosion*) and manifests itself in the form of an *abrupt singular jump* of the desorption flux relaxation rate. It has been shown [18, 19] that in the limit of large initial number of A–B pairs the annihilation catastrophe acquires a universal (independent of initial pair number) character and a scaling theory of the universal annihilation catastrophe has been given. A systematic theory of the formation of the annihilation catastrophe from a smooth initial distribution has been developed in recent work [20] where the dependence of the critical point on the initial pair number has been found and a complete picture of catastrophe universalization has been constructed.

In this review paper I first present the key features of the scaling theory of the formation of the universal annihilation catastrophe and demonstrate some results of extensive numerical calculations, then I describe the regularities of catastrophe universalization, and, finally, I discuss the conditions and possibilities for experimental observation of the annihilation catastrophe and point out some prospective lines for its modification.

2. Model

I 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 $X = \pm\ell (X \in [-\ell, \ell])$ and irreversibly desorb as a result of surface reaction $A_{\mathrm{ads}} + B_{\mathrm{ads}} \to AB$ with a rate proportional to the product of surface concentrations $I = \kappa c_{\mathrm{As}} c_{\mathrm{Bs}}$ [21] (figure 1). Because of planar spatial homogeneity the system is effectively one dimensional. The boundary conditions are determined from the equality of diffusion I^D and desorption I flux densities at the surface $I^D|_s = I$, i.e. it is assumed that the surface layer capacity can be neglected. According to [16, 18] after introducing index 'H' (*heavy*) for slower diffusing species and index 'L' (*light*) for a faster one, the problem of species evolution in the dimensionless units reads (by symmetry I consider the interval $[0, \ell]$ only)

$$\partial h/\partial \tau = \nabla^2 h, \qquad \partial l/\partial \tau = (1/p)\nabla^2 l, \tag{1}$$

$$\nabla h|_s = (1/p)\nabla l|_s = -h_s l_s, \tag{2}$$

with $\nabla(h, l)|_{x=0} = 0$ and initial conditions $h(x, 0) = h_0$ and $l(x, 0) = l_0$. Here $h(x, \tau) = c_H/c_*$ and $l(x, \tau) = c_L/c_*$ are the reduced concentrations, $\nabla \equiv \partial/\partial x$, $x = X/\ell \in [0, 1]$ is the dimensionless coordinate, $\tau = D_H t/\ell^2$ is the dimensionless time, $p = D_H/D_L \leqslant 1$ is

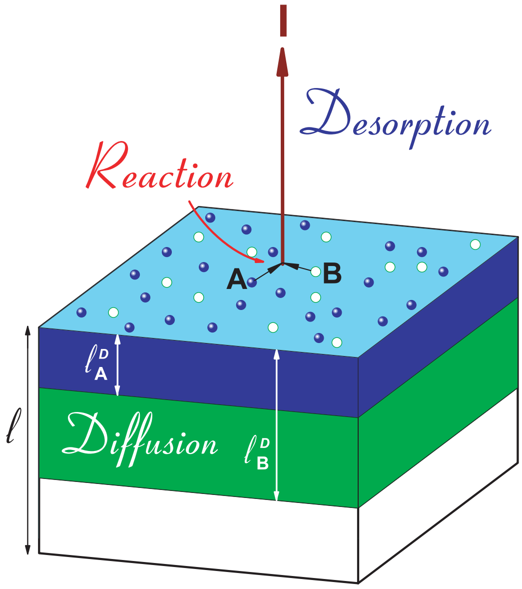


Figure 1. Schematic illustration of the processes of bulk diffusion, surface reaction and irreversible desorption in the system $A + B \to 0$. Because of planar spatial homogeneity the system is effectively one dimensional. $\ell_A^D = \sqrt{D_A t}$ and $\ell_B^D = \sqrt{D_B t}$ are the diffusion lengths of A and B particles, respectively.

the ratio of diffusivities and $c_* = D_H/\kappa\ell$ is the characteristic concentration scale. According to (2) particles disappear in pairs only, i.e.

$$J = h_s l_s = -\langle\dot{h}\rangle = -\langle\dot{l}\rangle,$$

where $J = I/I_*$ is the reduced desorption flux density and $I_* = \kappa c_*^2$ is its characteristic scale, therefore

$$\langle h\rangle - \langle l\rangle = \Delta = \text{const},$$

i.e. the excess amount stays 'inert' in the bulk (here $\langle h\rangle = \int_0^1 h\,\mathrm{d}x = \mathcal{N}_H/\mathcal{N}_*$ and $\langle l\rangle = \int_0^1 l\,\mathrm{d}x = \mathcal{N}_L/\mathcal{N}_*$ are the total reduced numbers of particles in the bulk per unit of surface and $\mathcal{N}_* = c_*\ell = D_H/\kappa$). This 'inert' part of the majority species $\Delta = \delta\mathcal{N}/\mathcal{N}_*$ acts as a control parameter, whereas its 'active' part $N = \mathcal{N}_{\text{pair}}/\mathcal{N}_*$ (equal to the total number of pairs) acts as the only variable. I will consider here the annihilation dynamics for $\Delta > 0$ when the pair number N is dictated by the number of L particles $N(\tau) = N_L(\tau)$ so that in the final state all L particles disappear $N(\infty) = l(x,\infty) = 0$ and H particles are distributed uniformly with concentration $h(x,\infty) = \Delta$. Moreover, I will focus mainly on the H-diffusion-controlled limit $N_0 \to \infty$ (note that the diffusion-controlled limit $N_0 = l_0 = c_L(0)/c_* \to \infty$ means $c_*^{-1} = \kappa\ell/D_H \to \infty$). Precisely in this limit the particle interplay is most 'intensive' and gives rise to the explosive dynamics that is my prime interest here.

3. Self-accelerating dynamics and the critical transition point

The exact formal solution of the problem (1), (2) in the Laplace space $\hat{f}(s) = \hat{\mathcal{L}}f(\tau)$ reads

$$\hat{h}(x,s) = h_0/s + \frac{(\hat{h}_s - h_0/s)\cosh(x\sqrt{s})}{\cosh(\sqrt{s})}, \qquad \hat{l}(x,s) = l_0/s + \frac{(\hat{l}_s - l_0/s)\cosh(x\sqrt{sp})}{\cosh(\sqrt{sp})}. \tag{3}$$

According to (3) the boundary conditions (2) acquire the form

$$\hat{J} = (h_0/s - \hat{h}_s)\sqrt{s}\tanh\sqrt{s} = (l_0/s - \hat{l}_s)\sqrt{s/p}\tanh\sqrt{sp} = \hat{\mathcal{L}}(h_s l_s) \tag{4}$$

and in an implicit form completely define the behaviour of surface concentrations h_s and l_s which in turn, via equations (3), define the evolution of spatial distribution. The strategy for solution of the nonlinear chain (4) is based on the fact that in the H-diffusion-controlled regime the $\frac{h_s}{\langle h\rangle}$ ratio should rapidly drop with the time, therefore, according to (4) we can first (i) calculate $J(\tau)$ and $l_s(\tau)$ neglecting the h_s contribution, then (ii) derive $h_s(\tau)$ from the condition $h_s = J/l_s$, and finally (iii) calculate next-to-leading terms, thereby defining the self-consistent picture of the evolution of surface concentrations.

3.1. Transient stage $\tau \ll 1$

At sufficiently small times the flux density is slightly changed, so assuming $J \approx J_0 = h_0 l_0$ from (4) one obtains

$$h_s = h_0(1 - v_h + \cdots), \qquad l_s = l_0(1 - v_l + \cdots) \tag{5}$$

where $v_i = \frac{2}{\sqrt{\pi}}\sqrt{\tau/\tau_i}$, $\tau_h = 1/l_0^2$ and $\tau_l = 1/ph_0^2$. According to (5) the relative drop rate for l_s and h_s is governed by the value of the parameter

$$R = v_l/v_h = r\sqrt{p}$$

where $r = h_0/l_0 = (1 + n_0)/n_0$ and $n_0 = N_0/\Delta$. So, the necessary conditions for the H-diffusion-controlled annihilation regime are fulfilment of the requirements $l_0 = N_0 \gg 1$ and $R < R_c = 1$. In [20] it is shown that for the condition $\epsilon = R_c - R \gg \tau_h^{1/4} = 1/\sqrt{N_0}$ at times $\tau \sim \tau_h$ the annihilation is followed by a sharp drop of h_s, crossing over to the H-diffusion-controlled regime, where the desorption flux density is governed by the rate of diffusion of H particles to the surface

$$J = h_0(1 - m)/\sqrt{\pi\tau} \approx J_0(\tau_h/\tau)^{1/2}/\sqrt{\pi}$$

with $m \sim (R/\epsilon^2)^2(\tau_h/\tau)$. In the region $\tau_h \ll \tau \ll p$ where both species diffuse in the semi-infinite medium regime from (4) it follows that

$$h_s = \frac{r}{\epsilon\sqrt{\pi\tau}}(1 - \phi + \cdots), \qquad l_s = l_0\epsilon(1 + \phi + \cdots) \tag{6}$$

where $\phi = (R/\sqrt{\pi}\epsilon^2)\sqrt{\tau_h/\tau}$. At sufficiently small p and not too large r (so that $R \ll R_c$) in the region $\tau_h, p \ll \tau \ll 1/r^2 < 1$ the distribution of L particles becomes uniform. In this regime from (4) it follows that

$$h_s = \frac{r}{\sqrt{\pi\tau}}(1 + \sigma + \cdots), \qquad l_s = l_0(1 - \sigma + \cdots), \tag{7}$$

where $\sigma = 2r\sqrt{\tau/\pi}$.

3.2. Exponential stage $\tau > 1$

According to equations (6) and (7) at large $N_0 \to \infty$, $\epsilon \gg 1/\sqrt{N_0}$ and not too large r (i.e. not too small n_0) by the moment that $\tau \sim 1$ when the diffusion length of H particles becomes comparable with the system's size, the ratio $h_s/h_0 \propto r/\epsilon N_0 \to 0$. Neglecting the contribution of h_s, it can be shown [20] that at $\tau > 1$ and large n_0 the value of h_s has to exponentially rapidly tend to a constant $\mathcal{C}$. In view of this, from (4) it follows that

$$J = \mathcal{A}e^{-\omega_0\tau}(1 + e^{-8\omega_0\tau} + \cdots), \tag{8}$$

where $\mathcal{A} = 2(h_0 - \mathcal{C}) \approx 2h_0$ and $\omega_0 = \pi^2/4$ is the main eigenfrequency of the diffusion field relaxation. With the same accuracy upon performing the inverse Laplace transform one obtains from (4) [20]

$$l_s = (\mathcal{A}/\Delta_c)\,\mathrm{e}^{-\omega_0\tau}(1-\Lambda), \tag{9}$$

where Δ_c is defined by

$$\Delta_c = \sqrt{\omega_0/p}\,\tan(\sqrt{\omega_0 p}) \tag{10}$$

and the leading contribution to Λ is governed by the sum of exponentially decaying, Λ_-, and exponentially growing, Λ_+, terms

$$\begin{aligned} &\Lambda = \Lambda_- + \Lambda_+, \\ &\Lambda_- = \varrho_8 \mathrm{e}^{-8\omega_0\tau} + \varrho_p \mathrm{e}^{-\chi\omega_0\tau}, \qquad \Lambda_+ = \lambda \mathrm{e}^{\omega_0\tau} \end{aligned} \tag{11}$$

with exponent $\chi = (4/p - 1)$ and amplitudes $\varrho_8 = -(\Delta_c/3)\sqrt{p/\omega_0}\cot(3\sqrt{\omega_0 p})$, $\varrho_p = (\Delta_c\sqrt{p}/\pi)\tan(\pi/\sqrt{p})$, and $\lambda = \Delta_c(\Delta - \mathcal{C})/\mathcal{A}$. From the condition $h_s = J/l_s$ and equations (8) and (9) locking the chain we find

$$h_s = \Delta_c(1 + \mathrm{e}^{-8\omega_0\tau} + \cdots)/(1-\Lambda). \tag{12}$$

3.3. Critical transition point

According to (11) and (12), in the limit of large $\frac{\mathcal{A}}{|\Delta - \mathcal{C}|\Delta_c} \to \infty$ ($|\lambda| \to 0$) the h_s value at *any* Δ exponentially rapidly achieves *universal* (Δ independent) asymptotics $h_s^c = \Delta_c$ whence it follows $\mathcal{C} = \Delta_c$. In view of (6), (7) and (12) it is easy to check [20] that the contribution of transient stage is reduced only to a relative shift of the amplitude $\delta\mathcal{A}_{\mathrm{tr}}/\mathcal{A}\,|_{h_0\to\infty} \sim r/\epsilon h_0 \to 0$, therefore with an accuracy of vanishingly small terms we finally have

$$\lambda = \Delta_c(\Delta - \Delta_c)/2h_0.$$

This important result implies that in the diffusion-controlled limit $N_0 \to \infty$ the critical asymptotic $h_s^c = \Delta_c$ appears as a *precursor* of long-time asymptotic $h_s|_{\tau\to\infty} = \Delta$, and precisely this intermediate asymptotic h_s^c *selects* the threshold value $\Delta = \Delta_c$ at the crossing of which the relaxation dynamics is qualitatively changed: at $\Delta < \Delta_c$ the surface concentration, h_s, escaping from h_s^c, decreases, reaching its limiting value Δ from *above*, whereas at $\Delta > \Delta_c$ the surface concentration, h_s, escaping from h_s^c, increases, reaching its limiting value Δ from *below*. Equations (8)–(12) and more detailed analysis in [16, 17] suggest that at the crossing of the threshold point $\Delta = \Delta_c$ not only the sign of $\dot{h}_s$ changes, but the growth of h_s (and with it the *whole annihilation process*) begins to accelerate autocatalytically as a result of 'switching-on' of the *loop of positive feedback*: diffusion-induced growth of h_s accelerates the drop of l_s, the drop of l_s accelerates the growth of h_s and so on (*self-accelerating death of pairs*). According to equations (11) and (12) for the time of the start of self-acceleration, τ_s, and the departure of the starting point $h_s^{\min}$ from the critical asymptotics h_s^c, $\delta_s = (h_s^{\min} - \Delta_c)/\Delta_c$, we find, respectively, $\tau_s = [1/\omega_0(\alpha+1)]\ln(\alpha\tilde{\varrho}/\lambda)$ and

$$\delta_s = (\alpha+1)\tilde{\varrho}^{\frac{1}{\alpha+1}}(\lambda/\alpha)^{\frac{\alpha}{\alpha+1}}, \tag{13}$$

where in the $0 < p < p_c = 4/9$ range $\alpha = 8$, $\tilde{\varrho} = 1 + \varrho_8$ whereas in the $p_c < p < 1$ range $\alpha = \chi$, $\tilde{\varrho} = \varrho_p$.

4. Annihilation catastrophe

The birth of an autocatalytic stage in the purely 'sink' system, which has been interpreted in [16] as a new type of self-organization, is the key point of the problem. In [18] it was shown that with growing Δ this stage becomes more and more pronounced so that far beyond the threshold self-acceleration acquires an *explosive* character: at $\Delta = \delta c(0)\kappa\ell/D_H \to \infty$ the rates of growth $\Omega_{Hs} = +\frac{\mathrm{d}\ln h_s}{\mathrm{d}\tau}$ and relaxation $\Omega_{Ls} = -\frac{\mathrm{d}\ln l_s}{\mathrm{d}\tau}$ are synchronized singularly growing by the law

$$\Omega_s = 1/|\mathcal{T}|, \qquad |\mathcal{T}| = |\tau - \tau_\star| \to 0,$$

where the point of *finite-time singularity* $\tau_\star$ is achieved at the moment when the reduced number of pairs $n(\tau) = N(\tau)/\Delta$ drops to some critical value $n_\star = \Delta_c/\omega_0 - 1 \approx p/(1-p)$. The most spectacular consequence of concentration explosion is the singular behaviour of the flux relaxation rate

$$\tau_J^{-1} = -\frac{\mathrm{d}\ln J}{\mathrm{d}\tau} = \Omega_{Ls} - \Omega_{Hs}$$

which is sustained at a constant value, $\tau_J^{-1} = \omega_0$, up to the critical point $\tau_\star$, and upon reaching this τ_J^{-1} blows up abruptly to $\tau_J^{-1} \to \infty$ with the width of the jump

$$|\mathcal{T}|_{\mathrm{cat}} \propto \Delta^{-2/5} \to 0.$$

In [18] it was shown that in the limit $n_0 = N_0/\Delta \to \infty$ this catastrophic jump of τ_J^{-1}, called the *annihilation catastrophe*, proceeds in the *universal* (n_0—independent) regime and the scaling theory of universal explosion was given. However, the approach developed in [18] did not allow one to say anything about the dynamics of explosion formation or about how the universal regime is achieved or how the point of catastrophe depends on the initial conditions.

I will follow here the work [20] where on the basis of equations (8)–(12) a closed theory of formation of the annihilation catastrophe has been developed. According to (4) and (12) the exponential growth $\delta h_s/h_s = \Lambda_+$ leads to an exponentially growing contribution to the flux $\delta J/J = -\beta\Lambda_+^2$ where $\beta \propto \Delta^{-1}$, suggesting that in the limit $\Delta \to \infty$ at the initial stage of self-acceleration the contribution to the flux is vanishingly small. The remarkable fact to be proved below is that at $\Delta \to \infty$ the contribution to the flux remains vanishingly small up to the point of finite-time singularity $\Lambda(\tau_\star) \to 1$ where $\dot{h}_s/h_s \to \infty$. This means that at $\Delta \to \infty$ equations (8)–(12) give a complete description of the explosion dynamics. Moreover, since at $\Delta \to \infty$ the parameter $\lambda = \Delta_c/2(1+n_0)$ becomes the unique function of $n_0 = N_0/\Delta$, equations (8)–(12) allow one to find the time of the catastrophe $\tau_\star(n_0)$ and to obtain the description of explosion evolution with growing n_0. Taking $\Lambda(\tau_\star) = 1$ and $\lambda < 1$ from equations (11) we find

$$\tau_\star = \tau_\star^u(1 + \delta_\tau), \tag{14}$$

where

$$\tau_\star^u = (4/\pi^2)\ln[2(1+n_0)/\Delta_c]$$

and

$$\delta_\tau(n_0) = -(\varrho_8\lambda^8 + \varrho_p\lambda^\chi)/|\ln\lambda|.$$

Taking then the origin of time at the point $\tau_\star$, i.e. introducing a relative time $\mathcal{T} = \tau - \tau_\star$, from equation (12) we find that at any $p < 1$ in the vicinity $|\mathcal{T}| \ll \omega_0^{-1}$ an explosive growth of h_s sets in by the law

$$h_s = (1+Q)/\mu|\mathcal{T}|, \qquad |\mathcal{T}| \to 0, \tag{15}$$

where $\mu = \frac{\omega_0}{\Delta_c} \sim 1 - p$ and $Q(n_0) = (1 + 9\varrho_8)\lambda^8 + (1 + \chi)\varrho_p\lambda^\chi$. According to equation (8) in the course of explosion the flux is actually 'frozen' $J = J_\star[1 + \omega_0(1 + w)|\mathcal{T}| + \cdots]$, reaching at the point of singularity the value

$$J_\star = \Delta\Delta_c(1 + G), \qquad |\mathcal{T}| \to 0, \tag{16}$$

where $w(n_0) = 8\lambda^8$ and $G(n_0) = (1 + \varrho_8)\lambda^8 + \varrho_p\lambda^\chi$. From equations (15) and (16) and the condition $h_s l_s = J_\star$ there immediately follows the synchronization of the growth, $\Omega_{Hs} = +\frac{\mathrm{d}\ln h_s}{\mathrm{d}\tau}$, and relaxation, $\Omega_{Ls} = -\frac{\mathrm{d}\ln l_s}{\mathrm{d}\tau}$, rates which singularly grow by the law

$$\Omega_s = \Omega_{Hs} = \Omega_{Ls} = 1/|\mathcal{T}|.$$

Clearly explosive growth of h_s^{ex} ought to trigger explosive growth of the 'antiflux' J_{ex}, the dominant contribution to which occurs in the vicinity $|\mathcal{T}| \ll 1$ where the diffusional response to the explosion forms in a narrow layer $\propto \sqrt{|\mathcal{T}|}$ [18]. Thus, considering the medium to be a semi-infinite one and allowing for (15) we can write [18, 20]

$$J_{\mathrm{ex}} = -\int_{-\infty}^{\mathcal{T}} \frac{\mathrm{d}h_s}{\mathrm{d}\theta}\frac{\mathrm{d}\theta}{\sqrt{\pi(\mathcal{T} - \theta)}} \sim -\frac{(1 + Q)}{\mu|\mathcal{T}|^{3/2}}$$

whence there follows smallness of $|J_{\mathrm{ex}}|/J_\star$ down to $|\mathcal{T}| \propto \Delta^{-2/3} \to 0$. Calculating then a singular contribution into the flux relaxation rate

$$\tau_J^{-1} = -\frac{\mathrm{d}\ln J}{\mathrm{d}\tau} = \omega_0(1 + w) + [\tau_J^{-1}] \tag{17}$$

we find

$$[\tau_J^{-1}] = -\dot{J}_{\mathrm{ex}}/J_\star \sim \frac{(1 + Q - G)}{\Delta|\mathcal{T}|^{5/2}} \tag{18}$$

whence there follows the *catastrophic jump* of τ_J^{-1} from $\tau_J^{-1} \approx \omega_0$ to $\tau_J^{-1} \to \infty$ with the width $|\mathcal{T}|_{\mathrm{cat}} \propto \Delta^{-2/5} \to 0$.

5. Scaling laws of passage through the point of singularity

According to [18], the remarkable consequence of the explosion in the limit $\mathcal{K} \sim p^{3/2}\Delta/\Delta_c \to \infty$ is the *exact scaling description* of passage through the point of singularity. I shall present here some basic results of the systematic scaling theory of annihilation catastrophe which I consider to be the most important analytical achievement. For simplicity, I shall begin with the universal limit $n_0 \to \infty$ and then, on its basis, a complete picture of catastrophe universalization with the growth of n_0 will be constructed.

Taking $\lambda, Q, G \to 0$, according to (8) and (9) at the explosion stage $\omega_0|\mathcal{T}| \to 0$ we have

$$J^{(0)} = J_\star(1 + \omega_0|\mathcal{T}| + \cdots), \qquad l_s^{(0)} = \mu J_\star|\mathcal{T}|(1 + \omega_0|\mathcal{T}|/2 + \cdots), \tag{19}$$

whence it follows that $h_s^{\mathrm{ex}} = J^{(0)}/l_s^{(0)} = 1/\mu|\mathcal{T}| + \cdots$, where the index '(0)' marks the solutions which neglect the contribution of $h_s = h_s^{\mathrm{ex}}$ ($h_s^{(0)} = 0$). As has been mentioned above, the explosive growth of h_s^{ex} ought to trigger the explosive growth of 'antiflux' J_{ex} in the calculation of which the medium can be regarded to be a semi-infinite one. So, the total flux $J = J^{(0)} + J_{\mathrm{ex}}$. As the diffusion fluxes of fast and slow particles must be equal, $J_L^D|_s = J_H^D|_s = J$, it is clear that against the background of dropping $l_s^{(0)}$ there must arise an explosive growth of l_s^{ex} which must initiate exactly the same 'antiflux' $J_{\mathrm{ex}}^L = J_{\mathrm{ex}}^H = J_{\mathrm{ex}}$. Assuming that at a developed explosion stage $\Omega_s p \gg 1$ the dominant contribution to J_{ex} occurs at times $|\mathcal{T}|/p \ll 1$, when for L particles the medium can be regarded to be semi-infinite, we can write [18, 20]

$$J_{\mathrm{ex}} = -\int_{-\infty}^{\mathcal{T}} \frac{\mathrm{d}h_s^{\mathrm{ex}}}{\mathrm{d}\theta}\frac{\mathrm{d}\theta}{\sqrt{\pi(\mathcal{T} - \theta)}} = -\int_{-\infty}^{\mathcal{T}} \frac{\mathrm{d}l_s^{\mathrm{ex}}}{\mathrm{d}\theta}\frac{\mathrm{d}\theta}{\sqrt{p\pi(\mathcal{T} - \theta)}} \tag{20}$$

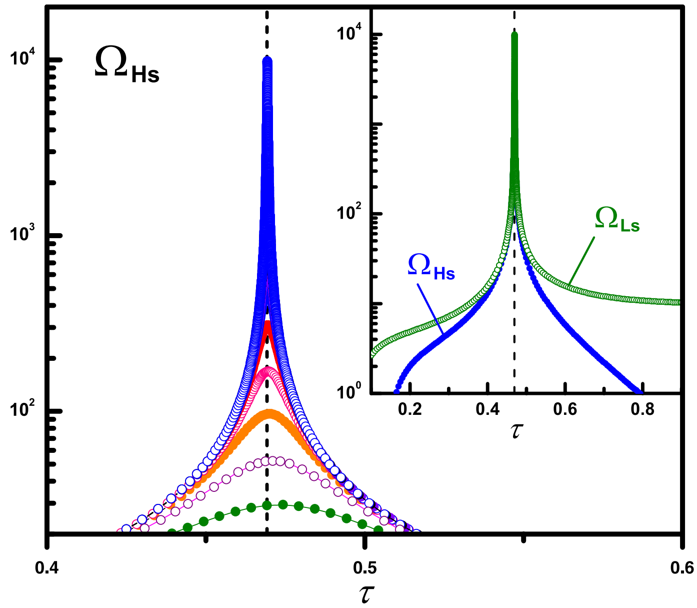


Figure 2. Formation of a singular concentration explosion with growing Δ at $n_0 = 4$ and $p = 0.25$. Shown (from bottom to top) are the dependences $\Omega_{Hs}(\tau)$ calculated numerically at $\Delta = 10^3, 3\times10^3, 10^4, 3\times10^4, 10^5, 3\times10^5, 10^6, 10^7$ and 10^8. The value of the critical point $\tau_\star$ calculated from equation (14) is denoted by the vertical dashed line. Inset: 'synchronization' of the concentration explosion in the vicinity of the critical point $\tau_\star$. Shown are the dependences $\Omega_{Ls}(\tau)$ and $\Omega_{Hs}(\tau)$ calculated numerically at $\Delta = 10^8$, $n_0 = 4$ and $p = 0.25$.

whence there follows *the key condition* of the scaling regime:

$$\sqrt{p}\dot{h}_s^{\rm ex} = \dot{l}_s^{\rm ex}. \tag{21}$$

Using (15) and (21) we obtain $l_s^{\rm ex} = \sqrt{p}h_s^{\rm ex} = \sqrt{p}/\mu|\mathcal{T}| + \cdots$ and then taking $l_s = l_s^{(0)} + l_s^{\rm ex}$ we conclude that in the vicinity of some characteristic time $\mathcal{T}_f \sim p^{1/4}/\mu\sqrt{J_\star}$ the explosive growth rate begins to drastically decelerate. Due to the requirement $\mathcal{T}_f/p \ll 1$ necessary for the realization of the regime (20), the explosive deceleration begins long before a noticeable flux departure from the critical one $|J_{\rm ex}(\mathcal{T}_f)/J_\star| \ll 1$. Introducing the parameter

$$\mathcal{K} = \mu^2 p^{3/2} J_\star$$

it can easily be seen that at any finite $0 < p < 1$ with growth of Δ in the limit of large $\mathcal{K} \sim p^{3/2}\Delta/\Delta_c \to \infty$ the ratio $|J_{\rm ex}(\mathcal{T}_f)|/J_\star \sim \sqrt{\mathcal{T}_f/p} \sim 1/\mathcal{K}^{1/4} \to 0$ and, therefore, down to $\mathcal{T}_f \to 0$ the flux remains 'frozen'. One of the most important consequences of the drastic deceleration of the explosive growth rate is the drastic deceleration of the rate of flux relaxation growth. In [18, 20] it is shown that in the limit of large $\mathcal{K} \to \infty$ as a result of such deceleration the flux remains 'frozen', and therefore the explosion develops synchronously

$$h_s l_s = J_\star, \qquad \Omega_s = \Omega_{Hs} = \Omega_{Ls} \tag{22}$$

both before and after passage through the point of singularity where Ω_s reaches a *maximum*. In figure 2 as an illustration I show the numerically calculated dependences $\Omega_{Hs}(\tau)$ that demonstrate the formation of singularity with growing Δ at $n_0 = 4$ and $p = 0.25$. An analysis of the given data suggests that as Δ grows, the critical point of the explosion maximum $\tau_\star(\Delta)$ rapidly ($\propto\Delta^{-1}$) comes to the point of singularity $\tau_\star(\infty)$, calculated according to equation (14).

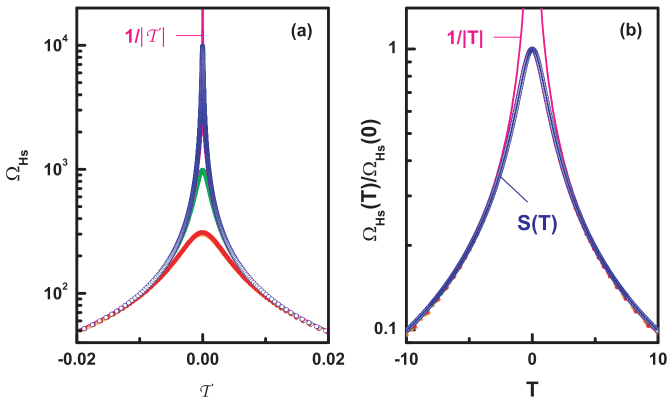


Figure 3. (a) Data of figure 2 for $\Delta = 10^5$, 10^6, 10^7 and 10^8 ($n_0 = 4$) replotted in the coordinates Ω_{Hs} versus $\mathcal{T}$, where $\mathcal{T} = \tau - \tau_\star$ and $\tau_\star$ is the point of the explosion maximum. The data of figure 8 ($\Delta = 10^5$) for $n_0 = 1.8$, 2.4 and 3.1 (diamonds) are also given. (b) Collapse of the data of (a) in scaling coordinates $\Omega_{Hs}(\mathsf{T})/\Omega^M_{Hs}$ versus $\mathsf{T} = \mathcal{T}\Omega^M_{Hs}$ to the scaling function $S(\mathsf{T})$ (solid line) calculated from equation (27).

In the inset the dependences $\Omega_{Hs}(\tau)$ and $\Omega_{Ls}(\tau)$ calculated numerically are compared at $\Delta = 10^8$. In accord with equations (22), at large Ω_s the curves are seen to merge in 'synchronous' explosion.

According to [20], combining equations (19), (21) and (22) enables one to obtain

$$\Omega_s(l_s + \sqrt{p}h_s) = \mu J_\star \tag{23}$$

whence there follows a *remarkably complete* scaling description of passage through the point of singularity. Indeed, from (22) and (23) we immediately conclude that the explosion rate goes through the maximum Ω^M_s in the point where $l^M_s/h^M_s = \sqrt{p}$, whence we derive

$$h^M_s = (2/\mu)\Omega^M_s = p^{-1/4}\sqrt{J_\star}, \qquad l^M_s = p^{1/4}\sqrt{J_\star}. \tag{24}$$

Introducing then the scaling function $\zeta = h_s/h^M_s = l^M_s/l_s$ from (23) and (24) we find [20]

$$\zeta - 1/\zeta = 2\Omega^M_s\mathcal{T}. \tag{25}$$

From equation (25) it is easy to see that the characteristic timescale of explosion is determined by the quantity $\mathcal{T}_f = 1/\Omega^M_s$, therefore introducing the reduced time $\mathsf{T} = \mathcal{T}/\mathcal{T}_f$ we finally obtain

$$\zeta(\mathsf{T}) = \mathsf{T} + \sqrt{1 + \mathsf{T}^2} \tag{26}$$

whence we derive the *scaling law of concentration explosion*

$$\Omega_s = \Omega^M_s S(\mathsf{T}), \qquad S(\mathsf{T}) = \frac{1}{\sqrt{1 + \mathsf{T}^2}}. \tag{27}$$

Two striking features of this result are the symmetrical universalization $|\mathcal{T}|^{-1} \leftrightarrow \mathcal{T}^{-1}$ of Ω_s beyond the scope of the interval $[-\mathcal{T}_f, \mathcal{T}_f]$ and the remarkable symmetry $\mathcal{T} \leftrightarrow -\mathcal{T}$, $\zeta \leftrightarrow 1/\zeta$. Figure 3(a) shows the data of figure 2 replotted in the coordinates $\Omega_{Hs}-\mathcal{T}$ where $\mathcal{T} = \tau - \tau_\star$, $\tau_\star$ being the point of the explosion maximum. It is seen that in full agreement with equation (27) (i) the rate of explosion $\Omega_{Hs}(\mathcal{T})$ demonstrates the *remarkable symmetry* $-\mathcal{T} \leftrightarrow \mathcal{T}$ and (ii) beyond the $[-\mathcal{T}_f, \mathcal{T}_f]$ region, with unlimitedly contracting with growth of Δ, the explosive rate comes to the *universal law* $1/|\mathcal{T}|$. In figure 3(b) the data of figure 3(a) are represented in the scaling coordinates $\Omega_{Hs}/\Omega^M_{Hs} - \mathsf{T}$ where $\mathsf{T} = \mathcal{T}/\mathcal{T}_f = \mathcal{T}\Omega^M_{Hs}$. It is seen that the numerically calculated dependences collapse perfectly to the scaling function $S(\mathsf{T})$ (27).

Substituting (26) into (20) allows one to find the scaling law of growth of the explosion-triggered 'antiflux' $J_{\mathrm{ex}} = J^M_{\mathrm{ex}}\mathcal{J}(\mathsf{T})$ and then obtain the singular part of the flux relaxation rate in the scaling form [18, 20]

$$[\tau_J^{-1}] = -\dot{J}_{\mathrm{ex}}/J_\star = [\tau_J^{-1}]_M W(\mathsf{T}) \tag{28}$$

where the amplitude at the point of explosion maximum

$$[\tau_J^{-1}]_M = c_M h^M_s (\Omega^M_s)^{3/2}/J_\star$$

and the scaling function

$$W(\mathsf{T}) = c_W \int_0^\infty \mathrm{d}\theta/\sqrt{\theta}[1 + (\mathsf{T}-\theta)^2]^{3/2}$$

has the asymptotics $W(\mathsf{T}) = (3\pi c_W/8)|\mathsf{T}|^{-5/2}, -\mathsf{T} \gg 1$ and $W(\mathsf{T}) = 2c_W\mathsf{T}^{-1/2}, \mathsf{T} \gg 1$, where $c_M = \frac{\Gamma^2(1/4)}{4\pi} \approx 1.046$ and $c_W = \frac{4\sqrt{\pi}}{\Gamma^2(1/4)} \approx 0.539$. Numerical analysis shows that at $\mathsf{T} = 0.462\,05$ the scaling function $W(\mathsf{T})$ reaches the maximum $\max W(\mathsf{T}) = 1.156\,27\ldots$ whence for the amplitude of catastrophe at the point of maximum we find

$$\max[\tau_J^{-1}] = (1.156\,27\ldots)[\tau_J^{-1}]_M.$$

Figure 4(a) demonstrates the dependences $\tau_J^{-1}(\mathcal{T})$ calculated numerically for the same parameters as in figure 3(a). The data analysis suggests that in accord with equations (17), (18) and (28) with growing Δ in the vicinity of the critical point $\tau_\star$ forms a *singular jump* of τ_J^{-1}, the width of which contracts unlimitedly by the law $|\mathcal{T}_{\mathrm{cat}}| \propto \Delta^{-2/5}$ and the amplitude of which grows unlimitedly by the law $\max\tau_J^{-1} \propto \Delta^{1/4}$ (see below). Based on the data of figure 4(a) in accord with equation (17) the time dependences of the singular part of the flux relaxation rate were calculated, $[\tau_J^{-1}](\mathcal{T}) = \tau_J^{-1}(\mathcal{T}) - \omega_0(1+w)$, and were then replotted in the scaling coordinates $[\tau_J^{-1}](\mathsf{T})/[\tau_J^{-1}](0) - \mathsf{T}$. The results are demonstrated in figure 4(b). It is seen that in perfect agreement with equation (28) with growing Δ the numerical results collapse to the scaling function $W(\mathsf{T})$. For a more detailed illustration in figures 4(c) and (d) the data of figure 4(b) are represented in double logarithmic coordinates in a wider range of $|\mathsf{T}|$ separately for $\mathsf{T} < 0$ (figure 4(c)) and $\mathsf{T} > 0$ (figure 4(d)).

Equations (24) and (26)–(28) give a detailed picture of the universal concentration explosion and annihilation catastrophe in the asymptotic limit $\mathcal{K} \to \infty$. Substituting into these expressions $J_\star = \Delta\Delta_c$ and marking the universal asymptotic values of amplitudes with the index (a) we obtain [18, 20]

$$h^M_s(a) = p^{-1/4}\sqrt{\Delta\Delta_c}, \qquad l^M_s(a) = p^{1/4}\sqrt{\Delta\Delta_c}, \tag{29}$$

$$\Omega^M_s(a) = (\mu/2)p^{-1/4}\sqrt{\Delta\Delta_c}, \tag{30}$$

$$[\tau_J^{-1}]_M(a) = (1.433\,40\ldots)p^{-5/8}\Delta_c^{-5/4}\Delta^{1/4}. \tag{31}$$

One of the remarkable analytical advantages of the above approach is that it enables one not only to determine the *exact asymptotic amplitudes* (29)–(31) but also to answer the question of *when and how* they are reached. A systematic analysis of the crossover to the asymptotics (29)–(31) is given in [20]. The central conclusion is that Ω^M_{Hs} reaches the asymptotic limit $\Omega^M_s(a)$ much faster than Ω^M_{Ls}, therefore *the point of the explosion maximum is defined by precisely by the point of the Ω_{Hs} maximum*. According to [20], with growing $\mathcal{K}$ the asymptotic amplitudes (30) and (31) are reached by the laws

$$\Omega^M_{Hs}/\Omega^M_s(a) = 1 - B_\Omega\mu/\mathcal{K}^{1/4} + O_\Omega(\mathcal{K}^{-1/2}), \tag{32}$$

$$\Omega^M_{Ls}/\Omega^M_s(a) = 1 + (c_M/\sqrt{2} - B_\Omega)\mu/\mathcal{K}^{1/4} + \cdots. \tag{33}$$

$$[\tau_J^{-1}]_M/[\tau_J^{-1}]_M(a) = 1 + B_J\mu/\mathcal{K}^{1/4} + O_J(\mathcal{K}^{-1/2}) \tag{34}$$

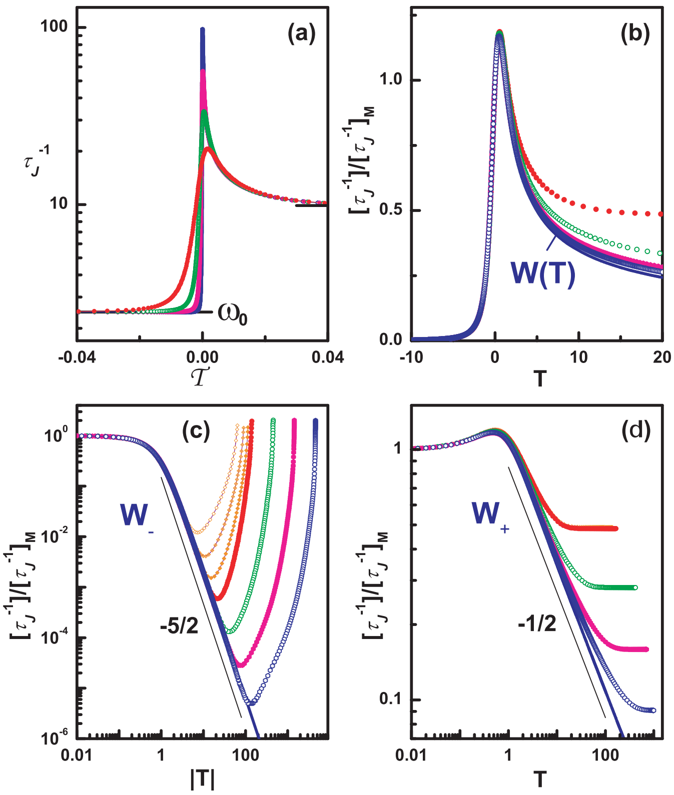


Figure 4. (a) Formation of a singular jump of the flux relaxation rate τ_J^{-1} with growing Δ at $n_0 = 4$ and $p = 0.25$. Shown are the dependences $\tau_J^{-1}(\mathcal{T})$ calculated numerically at $\Delta = 10^5, 10^6, 10^7$ and 10^8 (from left to right). (b) Collapse of the dependences $[\tau_J^{-1}](\mathsf{T})/[\tau_J^{-1}](0)$ versus $\mathsf{T} = \mathcal{T}\Omega_{Hs}^M$ calculated from the data of (a) to the scaling function $W(\mathsf{T})$ (solid line) calculated from equation (28). The singular part of the relaxation rate was calculated from equation (17). (c), (d) The data of (b) replotted in double logarithmic coordinates in a wider range of $|\mathsf{T}|$ for the ascending $\mathsf{T} < 0$ (c) and descending $\mathsf{T} > 0$ (d) catastrophe branches. The data based on numerical calculation for $n_0 = 1.8, 2.4$ and 3.1 ($\Delta = 10^5$, diamonds) which demonstrate the collapse to the scaling function $W(\mathsf{T})$ with growing n_0 are also given.

where $B_\Omega \approx 0.0318$ and $B_J \approx 0.776$. From these expressions we conclude that Ω_{Hs}^M always goes to its asymptotic *from below* whereas $[\tau_J^{-1}]_M$ and Ω_{Ls}^M always go to their asymptotics *from above*. Remarkably, the coefficient B_Ω appears to be *anomalously small* so that the contribution of the $\mathcal{K}^{-1/4}$ term in the case of Ω_{Hs}^M becomes less than 0.01 already at $\mathcal{K} > 10^2$.

To test the analytical predictions in [20] extensive numerical calculations were performed within $\Delta = 10^4$–10^8 for $p = 0.01, 0.03, 0.1, 0.25, 0.5, 0.75$. To exclude the contribution of the initial conditions, the initial number of particles n_0 was, depending on p, selected from the range $n_0 = 10$–200 so that in accord with equations (37) this contribution may not exceed $10^{-3}\%$. Figure 5 shows the numerically calculated dependences $\gamma_\Omega = \Omega_{Hs}^M/\Omega_s^M(a)$ and $\gamma_J = [\tau_J^{-1}]_M/[\tau_J^{-1}]_M(a)$ as functions of $\mathcal{K}/\mu^4$. It is seen that with growing $\mathcal{K}$ the numerically calculated amplitudes Ω_{Hs}^M and $[\tau_J^{-1}]_M$ come, respectively, to the asymptotic values $\Omega_s^M(a)$ and $[\tau_J^{-1}]_M(a)$ calculated analytically according to equations (30) and (31). Remarkably, in accord with the predictions of equations (32) and (34): (i) γ_Ω comes to 1 *from below* whereas γ_J comes to 1 *from above*; (ii) γ_Ω comes to 1 much faster than γ_J; (iii) the law by which γ_J

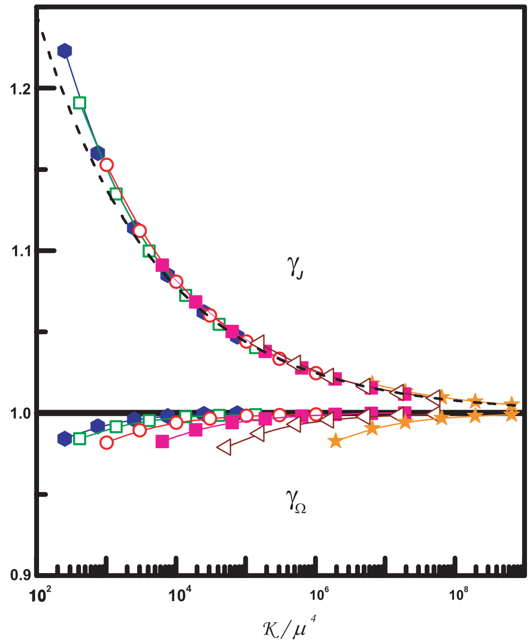


Figure 5. The regularities by which the universal amplitudes Ω_{Hs}^M and $[\tau_J^{-1}]_M$ approach the asymptotic values $\Omega_s^M(a)$ (equation (30)) and $[\tau_J^{-1}]_M(a)$ (equation (31)) with growing $\mathcal{K}$. Shown are the dependences $\gamma_\Omega = \Omega_{Hs}^M/\Omega_s^M(a)$ and $\gamma_J = [\tau_J^{-1}]_M/[\tau_J^{-1}]_M(a)$ versus $\mathcal{K}/\mu^4$ calculated numerically within $\Delta = 10^4$–10^8 for $p = 0.01, 0.03, 0.1, 0.25, 0.5$ and 0.75 (from left to right). Depending on p, the initial number of particles n_0 was selected from the range $n_0 = 10$–200. The analytical dependence $B_J\mu/\mathcal{K}^{1/4}$ (equation (34)) is shown by a dashed line.

approaches 1 in a wide range of $\mathcal{K}/\mu^4$ is described with excellent accuracy by the principal term of equation (34).

From equations (17), (18), (28) and (31) it follows that the *width* of the jump in the flux relaxation rate does not depend on p whereas its *amplitude*

$$\max \tau_J^{-1} \sim [\tau_J^{-1}]_M \propto p^{-5/8}(1-p)^{5/4}\Delta^{1/4}$$

grows rapidly with diminishing p. So, *the smaller p* is, i.e. the less L-diffusion restrains the development of the explosion, *the more brightly the effect is displayed*. It is clear, however, that in the limit of small $p \to 0$ the condition $\mathcal{K} \to \infty$ imposes a rigid requirement to the value Δ. In [18] it was demonstrated that if $\Delta \to \infty$ but $p \to 0$, so that $\mathcal{K} \ll 1$, the distribution of L species is retained uniform ($l_s = N, \Omega_{Ls} = h_s$) and the final stage of explosion is thus changed radically. It was discovered [18, 19, 22] that in the limit $\Delta \to \infty, \mathcal{K} \ll 1$ at the point of explosion maximum Ω_{Hs}^M an intermediate scaling should take place

$$h_s^M = q\Omega_{Hs}^M = b_H\Delta^{2/3}, \qquad l_s^M = b_L\Delta^{1/3}. \tag{35}$$

This prediction is supported by the numerical data which yield $q = 2.24$, $b_H = 1.63$ and $b_L = 0.73$ [18, 22]. From equation (35) it follows that at $\Delta \to \infty, \mathcal{K} \ll 1$ the jump amplitude of τ_J^{-1} at the explosion maximum grows with Δ much more sharply

$$[\tau_J^{-1}]_M = (q-1)\Omega_{Hs}^M \propto \Delta^{2/3}, \tag{36}$$

which gives rise to a qualitatively new phenomenon: the finite jump of the flux by a factor of $\approx$2 for the time $|\mathcal{T}|_{\mathrm{break}} \propto \Delta^{-2/3} \to 0$ (*flux breaking effect*). Leaving aside discussion of the crossover from the '*flux breaking*' regime to the '*synchronous explosion*' regime with growing $\mathcal{K}$ [22], I shall focus here on the key property of the annihilation catastrophe in the limit of small $p \to 0$. In accord with equation (28), in the limit $\mathcal{K} \to \infty$, after the critical point has been passed, the flux relaxation rate drops by the Δ-independent law $\propto 1/\sqrt{\mathcal{T}p}$, reaching at times $\mathcal{T} \sim p/\omega_0^2$ the L-diffusion-controlled limit ω_0/p [18]. Since in the limit $\mathcal{K} \ll 1$ the flux relaxation rate always grows with time, we conclude that *independently* of $\mathcal{K}$ in the limit $p \to 0$, $\Delta \to \infty$ there arises the most dramatic consequence of the annihilation catastrophe: *an abrupt, practically instantaneous* (on the scale of ω_0) *disappearance of the flux* [18, 19, 22] (figure 6).

6. Universalization of the annihilation catastrophe

In [20] it was shown that the scaling theory of the annihilation catastrophe, presented in the previous section for the universal limit $n_0 \to \infty$, also holds in the *general case* of finite n_0 and $\lambda < 1$ with the sole difference that now

$$J_\star(n_0) = \Delta\Delta_c[1 + G(n_0)] \qquad \text{and} \qquad [\Omega_s^M/h_s^M](n_0) = (\mu/2)[1 - Q(n_0)]$$

become the functions of n_0. We thus have the *complete scheme* to lock the chain (5)–(18) and to answer the question of *when and how* the universality is reached. It remains for us to find the central characteristic of scaling, namely the amplitude of the explosion $\Omega_s^M(n_0)$, and then from equation (28) to derive the amplitude of the catastrophe $[\tau_J^{-1}]_M(n_0)$. Using equations (24) we obtain

$$\Omega_s^M = \frac{\mu}{2}(1 - Q)h_s^M = \frac{\mu}{2}(1 - Q)p^{-1/4}\sqrt{J_\star}$$

whence we conclude that at $\lambda < 1$ evolution of explosion with growing n_0 *is completely defined* by functions $Q(n_0)$ and $G(n_0)$, and find finally the laws of universalization of amplitudes of explosion

$$\Omega_s^M(n_0) = \Omega_s^M(\infty)(1 + \delta_\Omega)$$

and catastrophe

$$[\tau_J^{-1}]_M(n_0) = [\tau_J^{-1}]_M(\infty)(1 + \delta_J)$$

in the form

$$\delta_\Omega = G/2 - Q, \qquad \delta_J = G/4 - 3Q/2. \tag{37}$$

I distinguish two main consequences of equations (37):

(1) According to (15) and (16) the drop of δ_Ω and δ_J with growing n_0 is *surprisingly rapid*:

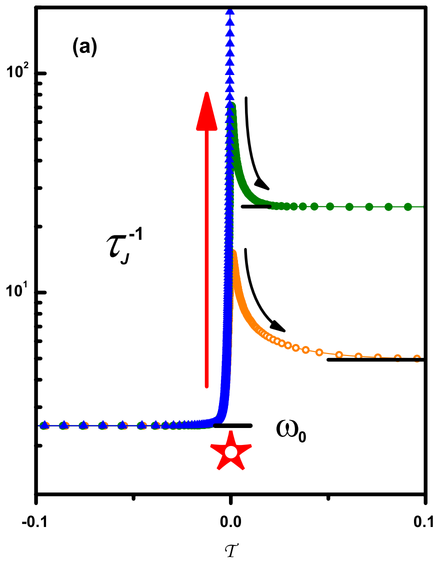
$$Q, G \propto n_0^{-8}(p < p_c), \qquad Q, G \propto n_0^{-\chi}(p > p_c),$$

where $3 < \chi(p) < 8$. Comparing this with the relatively slow decrease of δ_s (equation (13))

$$\delta_s(p < p_c) \propto n_0^{-8/9}, \qquad \delta_s(p > p_c) \propto n_0^{-\chi/(\chi+1)}$$

we conclude that universalization of explosion occurs *long before* $h_s^{\min}$ has reached h_s^c;

(2) According to (37) in the range $p < p_c$ with decreasing p some critical values $\varrho_{8,i}^*(p_i^*)$ are reached at which δ_Ω and δ_J reverse their sign $(- \to +)$ so that contrary to an intuitive reasoning at $p < p_\Omega^*$ and $p < p_J^*$ the amplitudes Ω_s^M and $\max\tau_J^{-1}$, respectively, *drop* with growing n_0. From (15), (16) and (37) we obtain $\varrho_{8,\Omega}^* = -1/17$, $p_\Omega^* = 0.0609$ and $\varrho_{8,J}^* = -5/53$, $p_J^* = 0.0217$. Note that this correlates with the behaviour of the function δ_τ that passes through zero $(- \to +)$ at $p_\tau^* = 1/9$.



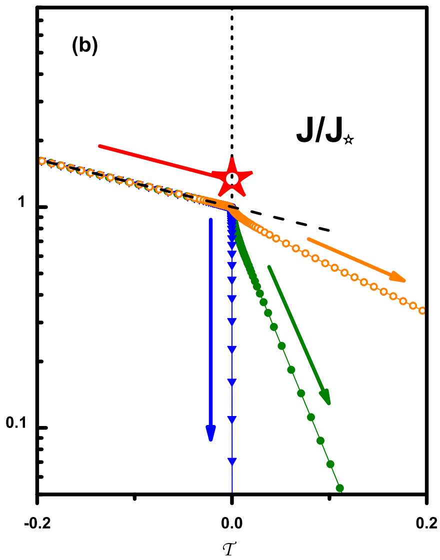


Figure 6. Annihilation catastrophe at different values of p. Shown are the time dependences $\tau_J^{-1}(\mathcal{T})$ (a) and $J(\mathcal{T})/\Delta\Delta_c$ (b) calculated numerically at $\Delta = 10^6$ and $n_0 = 10^2$ for $p = 0.5$ (open circles), $p = 0.1$ (filled circles) and $p = 10^{-6}$ (triangles). Note the abrupt disappearance of the flux at $p = 10^{-6}$.

Figures 7 and 8 show the results of numerical calculations for $\Delta = 10^5$ and $p = 0.25$, giving a detailed picture of the formation of the universal explosion with growing n_0. It is seen that in accord with equations (37) already at small departures from $n_0^c(R = R_c)$ the transient dynamics (7) terminates in an explosion that *remarkably rapidly* becomes universal: further growth of n_0 leads to a progressive shift of the critical point $\tau_\star(n_0)$ (figures 7(a) and 8) without changing the explosive dynamics in its vicinity but gradually universalizing *the entire self-acceleration trajectory* (figure 7(b)). I distinguish two important points which characterize the universalization process: (i) in accord with equations (27) and (28) a *symmetrical* 'flash' of the

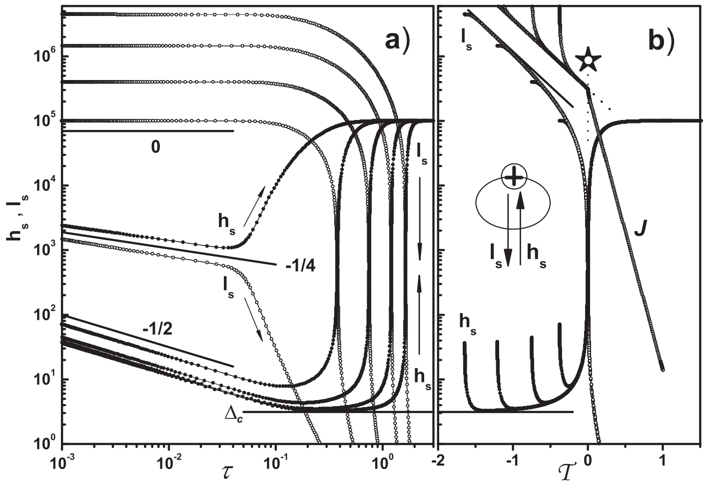


Figure 7. Formation of universal concentration explosion with growing n_0 at $\Delta = 10^5$ and $p = 0.25$. (a) Numerical calculation of the behaviour of $l_s(\tau)$ and $h_s(\tau)$ for $n_0 = 1 (R = R_c)$, 3, 9, 30, 90 (from left to right). (b) Data for $n_0 = 3$–90 replotted in $\log_{10}(l_s, h_s) - \mathcal{T}$ ($\mathcal{T} = 0$ corresponds to Ω^M_{Hs}). Also given are the data for the flux $J = h_s l_s$.

explosion rate Ω_{Hs} and an accompanying *sharply asymmetrical* jump of the flux relaxation rate τ_J^{-1} (figure 8) form *long before* the universalization of the corresponding amplitudes, shifting self-similarly with growing n_0; (ii) in accord with equations (13) and (17) as n_0 grows, the starting point of catastrophe reaches the level ω_0 (figure 8) *long before* the starting point of self-acceleration, $h_s^{\min}$, reaches the level Δ_c (figure 7). To test the analytical predictions I have numerically studied the behaviour of the dependences $\tau_\star(n_0)$, $\Omega^M_{Hs}(n_0)$, $[\tau_J^{-1}]_M(n_0)$ and $h_s^{\min}(n_0)$ by 'scanning' n_0 from n_0^c to 10^4 in wide ranges of $\Delta = 10^5$–10^8 and $p = 10^{-3}$–0.97 [20]. Based on the obtained data for each of the studied p and Δ values I calculated the dependences $\delta_\tau(n_0) = \tau_\star(n_0)/\tau_\star^u - 1$, $\delta_\Omega(n_0) = \Omega^M_{Hs}(n_0)/\Omega^M_{Hs}(\infty) - 1$, $\delta_J(n_0) = [\tau_J^{-1}]_M(n_0)/[\tau_J^{-1}]_M(\infty) - 1$ and $\delta_s(n_0) = h_s^{\min}(n_0)/\Delta_c - 1$ which I then compared with the analytical predictions. I have found that in the region of small $\delta_i(n_0)$ ($i = \tau, \Omega, J, s$) the behaviour of functions $\delta_i(n_0)$ is described with remarkable exactness by equations (14), (37) and (13). Figure 9 represents the concluding $n_0 - p$ *diagram of universalization* in which are compared the positions of the boundaries $|\delta_i| = 0.01$ ($i = \tau, \Omega, J$) and $\delta_s = 0.1$ resultant from a great number of numerical data (some of which are given in the inset) for $\Delta = 10^5$ (in the case $i = J$ for $\Delta = 10^7$) and calculated from (37), (14) and (12). Excellent agreement of the analytical and numerical results (*not shifting* with the further growing Δ) needs no comment.

7. Experimental observation

Let us discuss the conditions and possibilities of an experimental observation of the annihilation catastrophe. The irreversible bimolecular reaction $A + B \to 0$ is one of the most abundant reactions, therefore it is to be expected that the predicted phenomena can, in principle, be observed in a wide class of physical, chemical and biological systems with a 'catalytic' interface which, because of its high energetic barrier, does not let diffusing particles A go from medium 1 to medium 2 and diffusing particles B from medium 2 to medium 1 so that the reaction $A + B \to 0$ can occur *only at the interface between the media* [21, 23, 24]. Leaving aside here the discussion of such systems, I shall focus on the main object of the model in

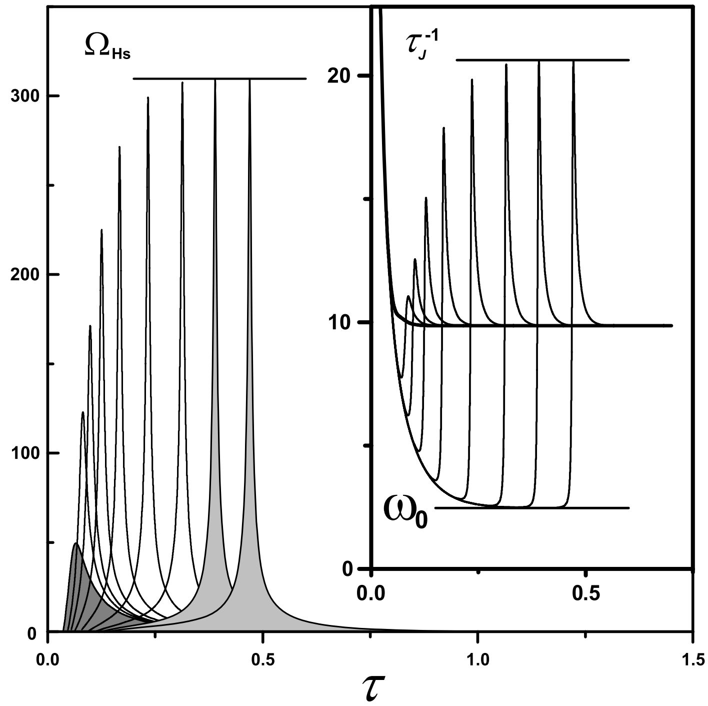


Figure 8. Evolution of $\Omega_{Hs}(\tau)$ (main panel) and $\tau_J^{-1}(\tau)$ (inset) with growing n_0 at $\Delta = 10^5$ and $p = 0.25$. The numerical calculation results are shown for $n_0 = 1 (R = R_c)$, 1.05, 1.1, 1.2, 1.4, 1.8, 2.4, 3.1, 4 (from left to right).

question, namely *adsorption–desorption* systems (figure 1). Until now most of the theoretical studies on the $A_{\rm ads} + B_{\rm ads} \to 0$ catalytic reaction (the Langmuir–Hinshelwood process which is also often referred to as the *monomer–monomer* catalytic scheme) have been performed under the assumption that diffusion into the bulk can be neglected ([25–35] and references therein). Such an assumption is valid in low-temperature systems with high surface–bulk crossover barriers, i.e. in systems with negligibly small bulk solubility of A and B particles. Here I address the wide class of catalytic systems where the surface–bulk crossover barriers are not too high and, therefore, adsorption–desorption processes are always followed by a more or less intensive diffusion of A and B particles into or from the bulk where reaction between A's and B's is energetically *forbidden* [36]. This class of catalytic systems is not only of fundamental interest for surface science but is also of considerable applied interest for describing the interaction kinetics of gases with metals at high temperatures ([36–39] and references therein). The theory presented in this paper gives a systematic description of the diffusion-controlled kinetics of associative desorption into a vacuum of unlike particles $A_{\rm ads}+B_{\rm ads} \to AB_{\rm gas} \to 0$, which are initially uniformly dissolved in the bulk. I shall focus here on discussing the possibility of observing the predicted effects for one of the *most important surface reactions*, carbon monoxide (CO) thermodesorption from metals into vacuum

$$C_{\rm ads} + O_{\rm ads} \to CO_{\rm gas} \to 0.$$

It is to be mentioned first that the continual description (1), (2) holds as long as the 'diffusion length' of the explosion at the point of maximum remains much greater than the monolayer thickness a [18], $\delta x_M \sim 1/\sqrt{\Omega_s^M} \gg a/\ell$, whence there follow the limitations

$$\Omega_s^M \ll (\ell/a)^2, \qquad \mathcal{K} \ll p^2(\ell/a)^4.$$

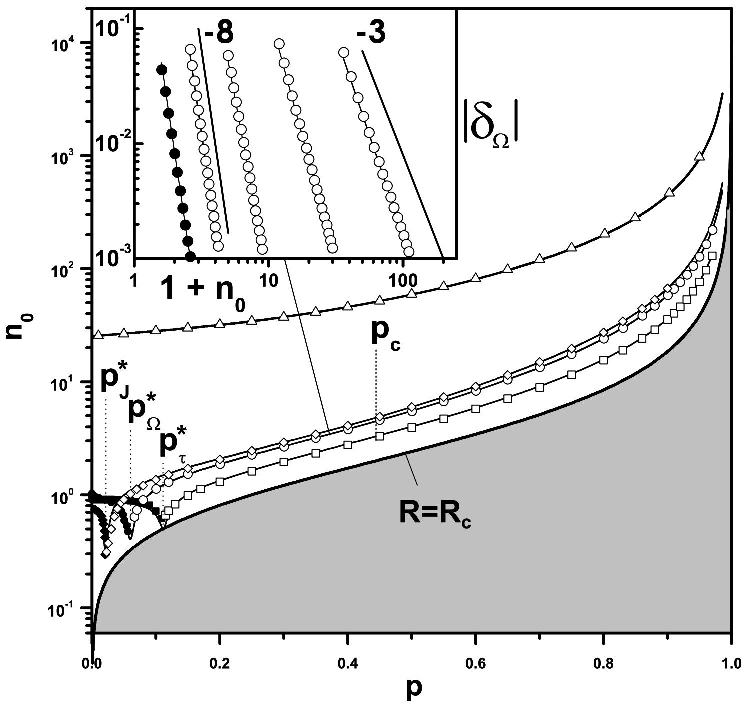


Figure 9. n_0–p diagram of universalization of concentration explosion and the annihilation catastrophe. Shown are numerically (symbols) and analytically (lines) calculated boundaries $|\delta_\tau| = 0.01$ (squares), $|\delta_\Omega| = 0.01$ (circles), $|\delta_J| = 0.01$ (diamonds) and $\delta_s = 0.1$ (triangles). Open symbols, $\delta_i < 0$; filled symbols, $\delta_i > 0$. Inset: numerically (circles) and analytically (lines) calculated dependences $|\delta_\Omega|$ versus $1 + n_0$ at $p = 0.01, 0.25, 0.5, 0.75$ and 0.9 (from left to right).

Taking, for example, $\ell/a \sim 10^3$ and $p \sim 0.01$ we come to the requirements $\Omega_s^M \ll 10^6$ and $\mathcal{K} \ll 10^8$ to see that for any value of the reaction rate constant κ the specimens must have macroscopic sizes in order a considerable effect be observed. Based on the data of monograph [37], I shall make estimations for three refractory metals, i.e. niobium, tantalum and molybdenum, which at elevated temperatures dissolve carbon and oxygen in quite large amounts. According to [37], at temperatures of intensive thermodesorption of CO in the range from $T \sim 1600\,^\circ\mathrm{C}$ to melting point for coefficients of carbon and oxygen diffusion in these metals we find, respectively, $D_\mathrm{C} \sim (10^{-7}$–$10^{-5})$ cm^2 s^{-1} and $D_\mathrm{O} \sim (10^{-5}$–$10^{-4})$ cm^2 s^{-1}, whence it follows $p = D_\mathrm{C}/D_\mathrm{O} \sim 10^{-2}$–$10^{-1}$. According to the data of [37–39] the desorption rate constant of CO in the said temperature range alters within $\kappa \sim (10^{-23}$–$10^{-18})$ cm^4 s^{-1}. Substituting these values into the expression

$$\Delta = \delta_\mathrm{C}(0)\kappa\ell/D_\mathrm{C}$$

and taking $\delta_\mathrm{C}(0) = c_\mathrm{C}(0) - c_\mathrm{O}(0) \sim 10^{20}$ cm^{-3} and $\ell \sim 0.1$ cm we find that in the said temperature range the Δ parameter value changes within $\Delta \sim 10^2$–10^6. For the density of the diffusion-controlled desorption flux of CO at the critical point we find $I_\star \sim D_\mathrm{C}\delta_\mathrm{C}(0)/\ell \sim 10^{14}$–$10^{16}$ particles cm^{-2} s^{-1}. We thus conclude that in a study of isothermal desorption of CO at elevated temperatures under high vacuum the predicted *sharp jump* of the flux relaxation rate can confidently be registered experimentally with a standard measuring technique.

8. Conclusion

In this paper the key features of the systematic theory of formation of the universal annihilation catastrophe from a smooth initial distribution have been presented and the results of extensive numerical calculations of the regularities of catastrophe formation in a wide range of parameters have been demonstrated. The two most important features of the annihilation catastrophe can be formulated as follows:

(1) In the majority of the models which demonstrate the formation of finite-time singularities an analytical description of the development of the singularity (based on properties of *self-similarity*) appears possible only for some narrow vicinity of the critical point beyond which the solution cannot as a rule be continued or is impossible in principle. One of the main advantages of the theory presented here is the asymptotically exact scaling description of passage through the point of singularity which yields a complete dynamical picture at the *both sides* of the critical point.

(2) Arising as a result of explosive growth of the 'antiflux' J_{ex} at the background of slow relaxation of the diffusion-controlled flux $J^{(0)}$, the annihilation catastrophe demonstrates a *peculiar singular behaviour* at which two explosive processes (Ω_{Hs} and Ω_{Ls}) are developing simultaneously, effectively 'compensating' one another, so that for an external observer of flux (J) the explosion dynamics *goes unnoticed* up to the critical point $\tau_\star$, in the vicinity of which 'decompensation' of explosions is manifested as a *sudden singular jump* of the flux relaxation rate. In the limit of small p this brings about a most radical consequence—*an abrupt disappearance* of the flux.

In conclusion, I would like to point out two of the many prospective lines of development of the results represented in this paper.

(i) *Fluctuations.* In recent works by O'Shaughnessy and Vavylonis [21, 23] it was shown that in the problem of diffusion-controlled interfacial annihilation $A + B \to 0$ the critical bulk dimension, below which fluctuation effects become essential, is $d_c = 1$. This implies that the quasi-one-dimensional mean-field theory represented here should give an adequate description of the development of the annihilation catastrophe in all physical dimensions $d = 3$ (catalytic surface), $d = 2$ (catalytic line) and $d = 1$ (catalytic point) with possible logarithmic corrections in the case $d_c = 1$. It should be noted, however, that the many-particle analysis performed in [21, 23] was carried out only for an initial transient stage of annihilation (semi-infinite medium). Therefore, it would be highly important (especially in the light of the recent work [40]) to carry out extensive numerical simulations of low-dimensional ($d = 1, 2$) discrete systems with the aim of revealing the role of fluctuation effects in the development of the annihilation catastrophe.

(ii) *Anomalous diffusion.* In the last few years much attention has been paid to researching reaction–diffusion systems with anomalous diffusion [14, 41, 42]. Subdiffusive motion is particularly important in the context of complex systems such as glassy and disordered materials. Recently, in [43] the scaling theory of *localized reaction front* propagation, introduced almost two decades ago by Galfi and Racz [10], was generalized for the case of a *reaction–subdiffusion* front. The scaling exponents of the front as functions of the subdiffusion parameter were obtained in the framework of the fractional dynamic approach and the quasistatic approximation (QSA). Note that according to the QSA the width and the height of the reaction front depend on time only through the diffusion (subdiffusion)-controlled boundary current J_f [44–47] which on the timescale of front equilibration remains effectively 'frozen', and in this sense it is analogous to the critical flux $J_\star$. Thus, on the basis of the scaling theory represented here and using a fractional dynamic approach it would be of great interest to study the laws of the formation of the annihilation catastrophe in systems with bulk subdiffusion.

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