

# Spatial and temporal asymptotic behavior of annihilation reactions

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The behavior of particles in a system over long intervals of time, of the domains of particles of a particular species, and of the particle distribution in the reaction near the domain walls is studied in the annihilation reaction  $A + B = 0$ .

In the present letter we consider the annihilation reaction between the particles of species  $A$  and  $B$  which diffuse in an inert medium. The particles  $A$  and  $B$  are the same in nature, there is no field effect, and the reaction is irreversible. The particles are initially distributed uniformly and in a completely random manner. The number of particles of one species is equal to that of the other. Systems corresponding to the description given above have been considered in Refs. 1 and 2.

Ovchinnikov and Zel'dovich<sup>3</sup> were the first to call attention to the unusual kinetics of such a reaction and Toussaint and Wilczek<sup>1</sup> studied this problem in-depth in a numerical experiment. Attention was drawn to the formation of 3D structures—domains occupied primarily by particles of a single species.

The behavior of the system is described by the equation

$$\dot{n}_{1,2} = D\Delta n_{1,2} - cn_1n_2 \quad (1)$$

where  $n_{1,2}$  are the densities of particles of species  $A$  and  $B$ ,  $D$  is the diffusion coefficient, and  $c = kDR_0^{d-2}$  is a coefficient which describes the reaction rate. Here  $R_0$  is the annihilation radius,  $d$  is the dimensionality of space, and  $k$  is a numerical coefficient which depends on the dimensionality of space and on the reaction probability. Introducing the variables  $r = n_1 - n_2$  and  $s = n_1 + n_2$ , we find

$$\begin{aligned} \dot{r} &= D\Delta r, \\ \dot{s} &= D\Delta s - \frac{c}{2}(s^2 - r^2). \end{aligned} \quad (2)$$

An important point here is that the first equation is a diffusion equation.<sup>3</sup> If the initial distribution of particles is completely random, the pairing correlation function is

$$G(\mathbf{x}, t) = \langle r(0, t)r(\mathbf{x}, t) \rangle = n_0 \frac{\Gamma(d/2)}{2^{3/2}\pi^d} (Dt)^{-d/2} \exp\left(-\frac{x^2}{8Dt}\right), \quad (3)$$

where  $\Gamma(z)$  is the gamma-function, and  $n_0 = \langle n_1(\mathbf{x}, 0) \rangle = \langle n_2(\mathbf{x}, 0) \rangle$  is the average initial particle concentration.

Let us consider the second equation. At the initial time we have  $s \gg r$ , so that after

short segments of time we have

$$\dot{s} = -\frac{c}{2}s^2 \text{ and } s = \left( \frac{1}{2n_0} + \frac{ct}{2} \right)^{-1}.$$

Since  $\langle r^2 \rangle = G(0, t) \sim t^{-d/2}$  decreases slower in the limit  $t \rightarrow \infty$  than it does at  $t^{-2}$ , at  $t > t_c \propto D^{d/(4-d)} c^{-4/(4-d)} n_0^{-2/(4-d)}$  we cannot ignore  $r^2$  in contrast with  $s^2$ . At  $t > t_c$ , there is a transition to another asymptotic regime. In the limit  $t \rightarrow \infty$  and  $d < 4$  we have  $\langle s^2 \rangle \sim \langle r^2 \rangle$  and  $\dot{s} \ll cs^2$ . We can find lower and upper estimates for  $\langle s(t) \rangle$  by setting  $D = 0$  and  $D = \infty$  in the second equation (independently of the first equation). In the first case we find  $s = |r|$  and  $\langle s \rangle = \langle |r| \rangle$  and in the second case we have  $\langle s \rangle = \langle r^2 \rangle^{1/2}$ . We thus find

$$\langle s(t) \rangle = \alpha \sqrt{G(0, t)} \sim t^{-d/4}; \quad \sqrt{2/\pi} \leq \alpha \leq 1. \quad (4)$$

Notice that the numerical coefficient  $\alpha$  changes by no more than 20% as a result of variation of the coefficient  $c$  in any range.

The reaction kinetics changes from  $t^{-1}$  to  $t^{-d/4}$  because of the formation of domains and because the reaction proceeds intensively only along the domain walls, i.e., along the lines (surfaces) of the level  $r = 0$ . The large-scale structure formed as a result of the reaction is determined by the structure of these lines of the level. Let us calculate, for example, the average size of a domain, defining it as the average length the sign of  $r(\mathbf{x}, t)$  remains constant along a straight line drawn randomly through the system. This length is

$$L(t) = \pi \sqrt{-\frac{dG(0, t)}{\Delta G(0, t)}}. \quad (5)$$

Equation (5) is a trivial generalization of the corresponding equation for the one-dimensional case.<sup>4</sup> In our problem  $L = 2\pi\sqrt{Dt}$ , in good agreement with the quantity which can be estimated from Fig. 5 of Ref. 1.

We now consider the particle density distribution in the reaction region near the domain walls. The width of this region is  $l \ll L$ . In this region the dynamic equilibrium between the diffusive influx of particles and their departure as a result of the reaction has time to establish itself. In the direction normal to the domain wall we have

$$\frac{d^2}{dz^2} s = \frac{c}{D} (s^2 - r^2), \quad (6)$$

where only the first term of the expansion  $r(z) = z \nabla r$  can be used near the line of the  $r = 0$  level. We can write the solution of (6) in the form

$$s(z) = a^{2/3} \left( \frac{c}{D} \right)^{-1/3} f \left[ \left( \frac{ac}{D} \right)^{1/3} z \right], \quad (7)$$

where  $f(\xi)$  is the solution of the equation  $f''(\xi) = f^2(\xi) - \xi^2$ , and  $a(\mathbf{x}, t)$  is the value of  $\nabla r$  at the domain wall. The distribution of  $a$  is a Gaussian distribution with the dispersion<sup>4</sup>

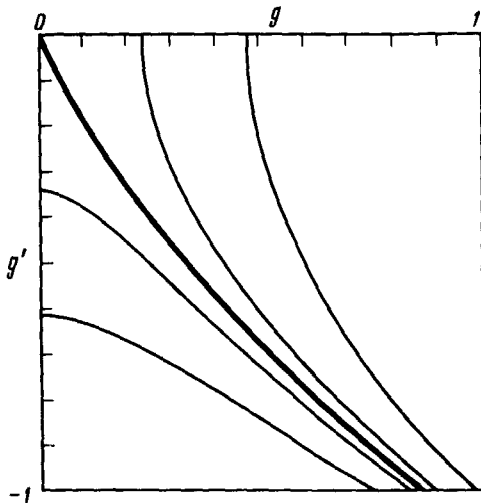


FIG. 1.

$$\sigma_a = \sqrt{-\Delta G(0, t)} = \sqrt{dG(0, t)/4Dt} \sim t^{-(d+2)/4}$$

The scale width of the domain wall,  $l = (ac/D)^{-1/3}$ , behaves as  $l \sim t^{(2+d)/12}$ , and at  $d < 4$  in fact increases slower than the domain.

The dimensionless deviation [measured in units of  $a^{2/3}(c/D)^{-1/3} \sim t^{-(d+2)/6}$ ] of  $s(z)$  from  $r(z)$  near the line of the  $r = 0$  level is described by the equation

$$g''(\xi) = g^2(\xi) + 2|\xi|g(\xi), \quad (8)$$

where the additional conditions  $g(\infty) = 0$  and  $g'(\pm 0) = \mp 1$ , which follow from the

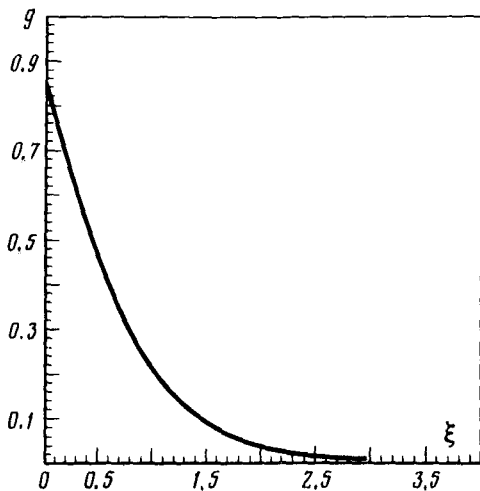


FIG. 2.

requirement that  $s(z)$  be smooth at the boundary, are imposed on the function  $g(\xi)$ . Analysis of the phase picture of Eq. (8) shows that the point (0,0) is a singular (saddle) point (see, e.g., Ref. 5). The trajectory which satisfies the additional conditions—the separatrix—is the only trajectory. The part of the phase picture with the relevant trajectory (the heavy line), which was obtained as a result of a numerical integration of (8), is shown in Fig. 1. The solution of (8) corresponding to the separatrix is shown in Fig. 2 for  $\xi > 0$ . The function  $g(\xi)$  is an even function.

Since at  $d < 4$  the width of the domain wall,  $l \sim t^{(2+d)/12}$ , increases slower than the domain itself,  $L \sim t^{1/2}$ , and since the concentration of the reacting particles at the domain wall,  $n_b \sim t^{-(d+2)/6}$ , decreases faster than the average concentration of these particles in the system,  $n \propto t^{-d/4}$ , the domain structure becomes more clearly defined with the passage of time. At  $d \geq 4$ , these relationships do not apply and total mixing sets in over time.

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<sup>1</sup>D. Toussaint and F. Wilczek, *J. Chem. Phys.* **78**, 2642 (1983).

<sup>2</sup>K. Kang and S. Redner, *Phys. Rev. B* **32**, 435 (1985).

<sup>3</sup>A. A. Ovchinnikov and Ya. B. Zel'dovich, *Chem. Phys.* **28**, 215 (1978).

<sup>4</sup>J. M. Ziman, *Disorder Models*, Russ. transl. Mir, Moscow, 1982.

<sup>5</sup>V. I. Arnol'd, *Ordinary Differential Equations*, Nauka, Moscow, 1975.