Diffusion-limited annihilation with initially separated reactants

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A diffusion-limited annihilation process $A+B\to\varnothing$ with species initially separated in space is investigated. A heuristic argument suggests the form of the reaction rate in dimensions less or equal to the upper critical dimension $d_c=2$. Using this reaction rate we find that the width of the reaction front grows as $t^{1/4}$ in one dimension and as $t^{1/6}(\ln t)^{1/3}$ in two dimensions.

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In this paper, we investigate the kinetics of diffusion-limited two-species annihilation process $A+B\to\varnothing$ in which collisions between two distinct species A and B lead to the formation of inert reaction products. Classically, such a process can be described by reaction-diffusion equations [1]

$$\frac{\partial a}{\partial t}=D\frac{\partial^2 a}{\partial x^2}-r,\quad \frac{\partial b}{\partial t}=D\frac{\partial^2 b}{\partial x^2}-r\ . \tag{1}$$

Here $a=a(x,t)$ and $b=b(x,t)$ are the local concentrations of A and B species, respectively, D is the diffusion coefficient, which is assumed to be identical for both species, and $r=r(x,t)$ is the reaction rate. In the mean-field approximation this reaction rate is proportional to concentrations of reactants $r=kab$. For sufficiently low dimensions, the diffusion mechanism is not efficient enough and fluctuations in the densities of diffusing reactants will result in a different form for the reaction rate and dimension-dependent kinetic behavior at long times [2].

Several recent studies have been focused on the situation in which species are initially separated in space and hence they react in a confined region called the reaction front. This front plays an important role for a variety of physical and chemical processes [3]. At the mean-field level, a scaling theory has been developed [4] that predicts that the width of the reaction front w grows in time as $t^{1/6}$ in agreement with experiments [5] and simulations [5–7].

Since the upper critical dimension for this process appears to be $d_c=2$ [7], a departure from the value $\alpha=\frac{1}{6}$ for the width exponent is expected for $d\le 2$. Numerical simulations of one-dimensional systems suggest the value $\alpha\approx 0.3$ [7–9]. However, an exact value of the width exponent in one dimension is unknown. In two recent works it was argued that $\alpha=\frac{1}{4}$ in one dimension. Both these studies are based on analysis of more tractable systems: the first paper [10] examines the case in which one reactant is static and other diffuses while the second paper [11] treats the behavior of the front in the steady state reached by imposing the antiparallel current densities of A and B species at $x=+\infty$ and $-\infty$, respectively. The latter steady state version of the original model was introduced in [12] and further explored in [13].

In the present study, we investigate the original transient problem of initially separated equally mobile species. Our analysis is based on the rate equations approach, but with a modified reaction rate. In one dimension, we find $\alpha=\frac{1}{4}$ in agreement with previous studies. In two dimensions we derive a logarithmic correction to the mean-field behavior: $w\sim t^{1/6}(\ln t)^{1/3}$. While it may be difficult to confirm this logarithmic correction numerically, a significant departure from the mean-field behavior, $w\sim t^{1/6}$, has been observed [7].

Let us first estimate the reaction constant k in the mean-field relation $r=kab$. It is reasonable to assume that the reaction constant depends on the diffusion constant D and the radius of particles R, which, for simplicity, is assumed to be the same for both species. Simple dimensional analysis gives $k\sim DR^{d-2}$. On physical grounds, the reaction constant must be an increasing function of the radius R and hence the previous expression for k is valid only for $d>2$. To find the reaction constant for $d<2$ we should assume that k does not depend on R, but instead it depends on concentrations $k=k(D,a,b)$. A dimensional analysis gives $k\sim D(a+b)^{-1+2/d}$ and therefore

$$r\sim Dab(a+b)^{-1+2/d}\ . \tag{2}$$

In fact, any symmetric function $r=r(a,b)$ of densities a and b with a degree of homogeneity $1+2/d$ is equally possible. However, in finding scaling exponents the precise form of the reaction term is unimportant and for concreteness we choose the form given above. Note that this simple dimensional argument also correctly predicts the value of the upper critical dimension $d_c=2$.

This type of argument was first applied by Toussaint and Wilczek [14] to homogeneous single-species annihilation $A+A\to\varnothing$ and led to the qualitatively correct long-time kinetic behavior $a\sim(Dt)^{-d/2}$ for $d<2$. In contrast, for homogeneous two-species annihilation $A+B\to\varnothing$ this argument predicts the incorrect value of the upper critical dimension (the correct value is $d_c=4$) and the incorrect kinetic behavior ($t^{-d/2}$ instead of $t^{-d/4}$; see [2,14]). Because of this difficulty there were no attempts to apply the argument to inhomogeneous two-species annihilation. It can be readily seen that a large-scale spatial organization of reactants [2,14] for homo-

geneous two-species annihilation leads to this difficulty. Indeed, the reaction takes place only near boundaries between different-species domains. The fraction of space occupied by these reaction zones tends to zero as $t \to \infty$ [15]. Hence modeling the reaction term by a function of *averaged* concentrations $a(t)$ and $b(t)$ is inappropriate since it gives the same reaction rate inside single-species domains where the reaction does not proceed and in the boundaries. However, for *inhomogeneous* two-species annihilation, the behavior in reaction zone where the reaction does proceed is of interest. Therefore, a description of reaction zone by using a (modified) reaction rate that is a function of local concentrations $a(x,t)$ and $b(x,t)$ seems reasonable.

Consider now a one-dimensional inhomogeneous system in which A particles are uniformly distributed to the right of the origin and B particles are uniformly distributed to the left of the origin, both with equal concentration c_0. The difference $a(x,t)-b(x,t)$ satisfies the diffusion equation, which, subject to given initial conditions, has the solution

$$a(x,t)-b(x,t)=c_0 \mathrm{erf}\left[\frac{x}{\sqrt{4Dt}}\right] . \tag{3}$$

In the long-time limit, the scaling form

$$\begin{aligned} a(x,t) &\sim t^{-\gamma}\mathcal{A}(xt^{-\alpha}) , \\ b(x,t) &\sim t^{-\gamma}\mathcal{B}(xt^{-\alpha}) , \\ r(x,t) &\sim t^{-\beta}\mathcal{R}(xt^{-\alpha}) \end{aligned} \tag{4}$$

is expected. Since $r \sim (a+b)ab$ in one dimension [see Eq. (2)], the scaling form of Eq. (4) implies the scaling relation $\beta=3\gamma$. Further, by inserting Eq. (4) into Eq. (2) and asymptotically balancing various terms one finds another scaling relation $\gamma+2\alpha=3\gamma$. Finally, assuming the reaction zone is short compared to the diffusion length $\sqrt{Dt}$ and making use of the exact solution (3) one gets $a-b \simeq c_0 x/\sqrt{\pi Dt} \sim t^{\alpha-1/2}$. This gives the last scaling relation $\alpha+\gamma=\frac{1}{2}$. Combining these scaling relations we find the exponents $\alpha=\gamma=\frac{1}{4}$ and $\beta=\frac{3}{4}$. Note that the width indeed increases slower than the diffusion length $w \sim t^{1/4} \ll t^{1/2}$, thus confirming our assumption. Rewriting the scaling ansatz in dimensionless form, we arrive at

$$\begin{aligned} a(x,t) &\simeq \left[\frac{c_0^2}{Dt}\right]^{1/4} \mathcal{A}(\xi) , \\ b(x,t) &\simeq \left[\frac{c_0^2}{Dt}\right]^{1/4} \mathcal{B}(\xi) , \\ r(x,t) &\simeq D\left[\frac{c_0^2}{Dt}\right]^{3/4} \mathcal{R}(\xi) , \end{aligned} \tag{5}$$

with the scaling variable $\xi=x(c_0^2/Dt)^{1/4}$.

Substituting Eqs. (5) into the governing equations (1) and making use of Eq. (3) we arrive at the still intractable nonlinear ordinary differential equation. However, if we focus on the region far enough from the origin $\xi \gg 1$, some progress can be made. To find the scaling form of densities we have to choose an appropriate form of the reaction rate. Let us mention that the reaction rate given by Eq. (2) at $d=1$, $r \sim Dab(a+b)$, has an additional advantage of being linear in concentration, which is small compared to the other, e.g., $r \sim Da^2 b \propto b$ if $b \ll a$. This physically appealing behavior suggests to use this particular form.

So, let us examine Eqs. (1) with the reaction rate

$$r=\kappa Dab(a+b) , \tag{6}$$

where κ is a dimensionless constant. In the region $(Dt/c_0^2)^{1/4} \ll x \ll \sqrt{Dt}$, where the A species dominates, Eq. (3) simplifies to $a \simeq c_0 x/\sqrt{\pi Dt}$, which can be rewritten as $\mathcal{A}(\xi) \simeq \xi/\sqrt{\pi}$ in the scaling form. Then the second Eq. (1) asymptotically reduces to

$$\frac{d^2\mathcal{B}}{d\xi^2}=\frac{\kappa}{\pi}\xi^2\mathcal{B} . \tag{7}$$

By applying the WKB procedure [16] one finds the asymptotic solution to Eq. (7),

$$\mathcal{B}(\xi) \sim \frac{1}{\sqrt{\xi}} \exp\left[-\left[\frac{\kappa}{4\pi}\right]^{1/2}\xi^2\right] , \tag{8}$$

which is valid for $\xi \gg 1$, i.e., for $x \gg (Dt/c_0^2)^{1/4}$. Combining Eqs. (5), (6), and (8) we arrive at the final asymptotic expression for the reaction rate:

$$r(x,t) \sim D\left[\frac{c_0^2}{Dt}\right]^{9/8} x^{3/2} \exp\left[-\left[\frac{\kappa}{4\pi}\right]^{1/2} x^2 \left[\frac{c_0^2}{Dt}\right]^{1/2}\right] \tag{9}$$

for $(Dt/c_0^2)^{1/4} \ll x \ll \sqrt{Dt}$.

Let us compare our prediction for the tail of the scaling distribution Eq. (9) with other studies. In a recent paper [8], the validity of the scaling distribution has been challenged and a description based on a continuous spectrum of scales between $t^{1/4}$ and $t^{3/8}$ has been proposed. In particular, Araujo *et al.* have fitted the tail of the reaction front by the exponential form $r \sim \exp[-|x|/t^{3/8}]$. In a very recent study [17], Cornell has reconsidered the problem. Based on extensive simulations he has found that the dynamical scaling appears to hold, contrary to the claim of Ref. [8]. He has obtained $\alpha \approx 0.28$ for the width exponent and observed that the reaction rate profile has a Gaussian form. Thus our results well agree with the most extensive present simulations [17].

Let us now turn to the two-dimensional version of the problem. The same line of reasoning gives the reaction rate $r \sim Dab$ and hence the mean-field behavior could be expected. However, $d=2$ is the marginal dimension, logarithmic corrections to mean-field expression $r \sim Dab$ may arise, and therefore one has to be more careful. To assess the validity of the mean-field expression for the reaction rate let us start from more fundamental relation $r \sim b/T$, where T is a time interval in which a B particle typically collides with some A particle. Consider for simplicity the region in which the A species dominates. In a reference frame at rest with respect to an arbitrary "target" B particle, the density $a(x+\mathbf{r},t+\tau)$ of A particles is governed by the diffusion equation

$$\frac{\partial a(x+\mathbf{r},t+\tau)}{\partial \tau}=2D\Delta_{\mathbf{r}}a(x+\mathbf{r},t+\tau)\ . \tag{10}$$

We should solve this equation subject to the initial condition $a(\tau=0)=a(x,t)$ [since the local density is $a(x,t)$] and the adsorbing boundary condition $a(|\mathbf{r}|=2R)=0$ for $\tau>0$. When $D\tau\gg R^2$, an approximate solution to Eq. (10) with prescribed initial and boundary conditions can be readily found by using a quasistatic approximation (see, e.g., [18]). This solution reads

$$a(x+\mathbf{r},t+\tau)\simeq a(x,t)\frac{2\ln(r/2R)}{\ln(D\tau/R^2)}\ . \tag{11}$$

Note that the "local" density given by Eq. (11) is changed on the length scale of the order $\sqrt{D\tau}$, which has to be small compared to the length scale of the "external" density $a(x,t)$, i.e., $\sqrt{D\tau}\ll w$. We will assume that both inequalities $R^2\ll\sqrt{Dt}\ll w$ hold and therefore Eq. (11) may be applied to estimate the collision time T. From the final expressions for T and w it is straightforward to verify that previous inequalities are indeed satisfied in the long-time limit, thus providing the check of self-consistency.

The collision time T may be evaluated by computing the flux to the circle of radius $2R$ and then by equating the flux to the unity

$$8\pi DR\int_0^T\frac{\partial a(|\mathbf{r}|=2R,t+\tau)}{\partial r}d\tau=1\ . \tag{12}$$

By combining Eqs. (12) and (11) one gets the final estimate $T\simeq\ln(1/8\pi aR^2)/8\pi Da$. Thus we obtain the expression for the reaction rate

$$r=8\pi Dab\left[\frac{1}{\ln(1/8\pi aR^2)}+\frac{1}{\ln(1/8\pi bR^2)}\right]\ . \tag{13}$$

The second term is added to keep $r=r(a,b)$ symmetric. In the region $x\gg w$, which we have considered, the second term is small and thus never appeared. Similarly, in the region $-x\ll -w$ the first term is negligible. Since the reaction rate must be symmetric function of the densities, Eq. (13) provides a proper combine approximation in both tail regions. It is therefore reasonable to assume that Eq. (13) is in fact accurate everywhere in reaction zone. So instead of the mean-field expression for the reaction rate in two dimensions $r=Dab$, a refined argument gives a logarithmically corrected value (13).

Now let us try a scaling ansatz

$$\begin{aligned}
a(x,t)&\simeq\left[\frac{c_0^2}{Dt}\right]^{1/3}L^{\mu}\mathcal{A}(\xi)\ ,\\
b(x,t)&\simeq\left[\frac{c_0^2}{Dt}\right]^{1/3}L^{\mu}\mathcal{B}(\xi)\ ,\\
r(x,t)&\simeq D\left[\frac{c_0^2}{Dt}\right]^{2/3}L^{\nu}\mathcal{R}(\xi)\ ,\\
\xi&=x\left[\frac{c_0^2}{Dt}\right]^{1/6}L^{\lambda}\ ,
\end{aligned} \tag{14}$$

where we have used a shorthand notation L for the logarithmic factor $L=\ln(Dt/c_0^2R^6)$. Equation (14) is just the standard mean-field scaling ansatz [4] modified by logarithmic corrections. A procedure identical to the one used in the one-dimensional situation gives three scaling relations between "logarithmic" exponents λ, μ, and ν from which one finds $\lambda=\nu=-\frac{1}{3}$ and $\mu=\frac{1}{3}$.

The main lesson from this study is the following: Even for sufficiently low dimensions $d\le d_c$, when the strong correlations destroy the mean-field approximation, it is still possible to use mean-field-like diffusion-reaction equations with modified reaction rates. At the critical dimension, the present heuristic method gives subtle logarithmic corrections, which seem hard to obtain by more solid theoretical approaches.

Let us finally mention that the more general higher-order annihilation reaction process $mA+nB\to 0$ with initially separated species can be analogously investigated by the present approach. Since the critical dimension for this reaction process is $d_c=2/(m+n-1)$ (see, e.g., [11]), deviations from the mean-field predictions are expected only for the classic case $(m,n)=(1,1)$ (when $d=1$ and 2) and for $(m,n)=(2,1)$ (when $d=d_c=1$). Consider the latter case and assume that pointlike particles undergo a random walk on the linear lattice with spacing Δx. (Even in one dimension we must keep the lattice spacing finite since otherwise the reaction with three-particle interaction is absent.) Focus again on the region where the A species dominates and estimate the collision time T. Note that the collision event, i.e., the situation when two A particles will be simultaneously in the site with a target B particle, may be described as usual two-body collision between an immobile target particle and imaginary particles corresponding to *pairs* of A particles and diffusing on the two-dimensional square lattice with the same spacing Δx. A more detailed description of this correspondence is given in Ref. [19], which considers a related single-species aggregation process $A+A+A\to A$. Then up to the replacement of the one-dimensional density a by the two-dimensional density of pairs a^2 and the spacing Δx by the radius R one can use previous results [see Eqs. (10)–(12)] and find the collision time $T\simeq\ln(1/8\pi a^2\Delta x^2)/8\pi Da^2$. So we obtain $r\sim Da^2b/\ln(1/a\Delta x)$ while the mean-field approach would give $r\sim Da^2b$. This results in logarithmic corrections to the mean-field behavior. Repeating the steps employed for the previous treatment of two-particle annihilation we arrive at the scaling form

$$\begin{aligned}
a(x,t)&\sim(L/t)^{1/4}\mathcal{A}(\xi)\ ,\\
b(x,t)&\sim(L/t)^{1/4}\mathcal{B}(\xi)\ ,\\
r(x,t)&\sim t^{-3/4}L^{-1/4}\mathcal{R}(\xi)\ .
\end{aligned} \tag{15}$$

Here $\xi=x(c_0^2/DtL)^{1/4}$ is the scaling variable and $L=\ln(Dt/c_0^2\Delta x^4)$ the logarithmic factor. Thus we conclude that the width of the reaction front for the three-particle reaction process $2A+B\to\varnothing$ scales as $t^{1/4}(\ln t)^{1/4}$ in one dimension.

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