Segregation in the static pair annihilation process: Exact results

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We study the one-dimensional pair annihilation process $A+B\rightarrow 0$, where the particles, which are initially distributed at random, interact in the absence of diffusion through a tunneling law. Monte Carlo simulations indicate that the large-time behavior of this process can be obtained from a staggered version of this model that can be exactly solved. Analytic expressions for the asymptotic decay of the reactant concentration and for the spatial pair correlations are given. Their agreement with the segregation pattern found in the simulations is checked.

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The tendency to self-organization is known to appear in various disordered systems submitted to stochastic dynamics [1]. In particular, for diffusion-limited reactions the relatively small density fluctuations may evolve into relatively large long-time density fluctuations. The usual kinetic reaction schemes which do not embody spatial fluctuations are not appropriate to describe the evolution of such systems at large time and low dimensionality, where the segregation phenomenon is strong. Several attempts have been made to find an analytical approach to the problem, and some exact solutions are known for one-dimensional systems [2–8].

A dynamical self-ordering is also known to appear when A-A or A-B annihilation occur through a tunneling law between immobile reactants [9,10]. In contrast with the diffusive case, analytical results are still lacking, in spite of the remarkable numerical observation made in Ref. [9] that a Kirkwood approximation, which we specify later on, provides the correct AB particle segregation pattern and the long-time asymptotic behavior of the reaction.

More specifically, as in Ref. [9], we consider the static annihilation (SA) process where randomly distributed A and B particles with equal initial concentrations annihilate through the reaction $A+B\rightarrow 0$ with a probability rate given by $w(r)=w_0\exp(-r/r_0)$. We specialize to the one-dimensional case; r is the A-B particles separation and r_0 is a scaling constant. Both A and B particles have at any time the same density $\rho(t)$ and there are only two pair correlations $X(r,t)$ and $Y(r,t)$. These are defined as statistical averages of the microscopic A,B particle densities $n_{A,B}(r,t)$:

$$\begin{aligned}&\rho(t)=\langle n_A(r,t)\rangle=\langle n_B(r,t)\rangle\ ,\\ &\rho^2(t)X(r_2-r_1,t)=\langle n_A(r_1,t)n_A(r_2,t)\rangle\\ &\qquad\qquad=\langle n_B(r_1,t)n_B(r_2,t)\rangle\ ,\\ &\rho^2(t)Y(r_2-r_1,t)=\langle n_A(r_1,t)n_B(r_2,t)\rangle\ .\end{aligned}\tag{1}$$

The decay of the density is thus given by $d\rho(t)/dt=-\rho^2(t)\int_{-\infty}^{\infty}w(r)Y(r,t)dr$ and more generally the kinetics obeys an infinite hierarchy of coupled differential equations for the many-point densities [1]. The mean-field approximations $X=Y=1$ or $X=1$, $Y=\exp[-w(r)t]$, which imply, respectively, $\rho(t)\sim t^{-1}$ and $\rho(t)\sim\ln^{-1}t$ at large time, appear to be valid only in the early stage of the process. According to Ref. [9], an appropriate approximation seems to be a Kirkwood superposition of the form

$$\begin{aligned}&\langle n_A(r_1,t)n_A(r_2,t)n_B(r_3,t)\rangle\\ &\qquad\simeq\rho^3(t)X(r_2-r_1,t)Y(r_3-r_1,t)Y(r_3-r_2,t)\ ,\end{aligned}\tag{2}$$

which reduces the infinite hierarchy to a closed, integral, nonlinear subsystem for ρ, X, and Y. In Ref. [9], the numerical solutions of this system are compared to the Monte Carlo (MC) simulation of the SA process. Their agreement is strikingly good with, in particular, the following results at large time:

$$\rho(t)\sim(\ln w_0 t)^{-1/2}\tag{3}$$

and

$$Y(r,t)\simeq\Theta(r-\xi(t))\tag{4}$$

where Θ is the step function and $\xi(t)$ the reaction radius defined by $w(\xi)t=1$.

The purpose of this work is to provide a more detailed understanding of the approach successfully initiated in Ref. [9], as a generalization of what we have recently done for the $A+A\rightarrow 0$ reaction [11]. Our starting observation, borrowed from expression (4), is that at time t all the pairs AB up to separation $\xi(t)$ have disappeared, the remaining ones being little affected. This suggests considering the following static staggered annihilation (SSA) model. As in the SA process, A and B particles are randomly deposited with equal concentrations on the sites of a one-dimensional lattice of unit spacing. But then, the $A+B\rightarrow 0$ reactions occur through a cascade of successive stages. In the first stage, all pairs of AB neighbors are randomly destroyed; in the second stage, all pairs of next-to-nearest neighbors AB vanish, and so on. Inside any stage, the decay evolves sequentially in terms

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of some internal time τ which runs from 0 to infinity and the initial conditions entering into a new stage are given by the final configurations of the system in the previous stage. As we shall see below, it is possible to solve the dynamics in any stage and to sum up an arbitrary number J of stages so as to give analytic expressions for the density and the correlations. Our statement is that the SSA and the SA models are asymptotically equivalent under the identification $J=\xi(t)$. This is quite natural since during the stage J the reacting pairs have separation J, and is perfectly supported by the Monte Carlo simulations of the SA model we have performed.

In order to solve the dynamics during an arbitrary stage j, we observe that no particle can survive between the two members of an annihilating pair, and thus any surviving particle separates the lattice into left and right uncorrelated sublattices. The probability of any configuration is then a product of pair probabilities. For example, $P_{AAB}(r_1,r_2,z)$ is the probability to observe at time $z=e^{-\tau}$ the sequence A_1A_2B, where r_1 is the A_1A_2 separation and r_2 the A_2B one, then

$$P_{AAB}(r_1,r_2,z)=P_{BBA}(r_1,r_2,z)=\rho(z)\gamma(r_1,z)\mu(r_2,z) , \quad (5)$$

where $\rho(z)$ is the A or B density and $\gamma(r,z)$ and $\mu(r,z)$ are defined through

$$\begin{aligned} &P_{AA}(r,z)=P_{BB}(r,z)=\rho(z)\gamma(r,z) , \\ &P_{AB}(r,z)=\rho(z)\mu(r,z) . \end{aligned} \quad (6)$$

The three-particle factorizations of the form (5), which are exact for the one-dimensional SSA model, play the role of the Kirkwood approximation (2), and are at the root of its solvability. It is sufficient to know ρ, γ, and μ whose evolution during the stage j can be derived from the following master equations:

$$z\partial_z\rho(z)=2P_{AB}(j,z) ,$$

$$z\partial_z P_{AA}(r,z)=\begin{cases} 2P_{AAB}(r,j,z) ; & r\le j \\ 2P_{AAB}(r,j,z)+2P_{ABA}(r-j,j,z) , & r>j , \end{cases} \quad (7)$$

$$z\partial_z P_{AB}(r,z)=\begin{cases} P_{AB}(j,z)+2P_{ABA}(j,j,z) , & r=j \\ 2P_{ABA}(r,j,z)+2P_{ABB}(j,r-j,z) , & r>j , \end{cases}$$

where the right-hand members show the various ways of destroying a particle through some pair interaction at distance j. Inserting the relations (5) and (6) in (7), one obtains

$$\begin{aligned} &z\partial_z\rho(z)=2\rho(z)\mu(j,z) , \\ &z\partial_z\gamma(r,z)=\begin{cases} 0 , & r\le j \\ 2\mu(r-j,z)\mu(j,z) , & r>j , \end{cases} \\ &z\partial_z\mu(r,z)=\begin{cases} \mu(j,z) , & r=j \\ 2\mu(j,z)\gamma(r-j,z) , & r>j . \end{cases} \end{aligned} \quad (8)$$

Thus

$$\begin{aligned} &\mu(j,z)=\omega_j z , \\ &\rho(z)=\rho(1)e^{2\omega_j(z-1)} , \end{aligned} \quad (9)$$

where ω_j is a stage factor $\omega_j=\mu(j,z=1)$ that will be determined below. For the correlations it is convenient to introduce their generating functions $\tilde\gamma(x,z)=\sum_{r\ge1}x^r\gamma(r,z)$ and $\tilde\mu(x,z)=\sum_{r\ge1}x^r\mu(r,z)$. In fact, $\mu(r,z)=0$ for $1\le r<j$ since all AB pairs at distance $r<j$ have been destroyed in the previous stages and thus

$$\tilde\mu(x,z)=x^j\omega_j z+\sum_{r>j}x^r\mu(r,z) . \quad (10)$$

From (8) and (9), one gets

$$\begin{aligned} &\partial_z\tilde\gamma(x,z)=2x^j\omega_j\tilde\mu(x,z) , \\ &\partial_z\tilde\mu(x,z)=x^j\omega_j+2x^j\omega_j\tilde\gamma(x,z) , \end{aligned}$$

which is diagonalized by $\alpha^{\pm}(x,z)=\frac{1}{2}+\tilde\gamma(x,z)\pm\tilde\mu(x,z)$ with the solution

$$\alpha^{\pm}(x,z)=\alpha^{\pm}(x,1)e^{\pm2x^j\omega_j(z-1)} . \quad (11)$$

We are now in position to sum up all the stages. With the notation ρ_{j-1}, $\alpha^{\pm}_{j-1}(x)$ for the density and the correlation functionals at the beginning of the stage j and ρ_j, $\alpha^{\pm}_j(x)$ at its end, expressions (9) and (11) give $\rho_j=\rho_{j-1}e^{-2\omega_j}$ and $\alpha^{\pm}_j(x)=\alpha^{+}_{j-1}(x)e^{\mp2\omega_j x^j}$. Thus

$$\rho_j=\rho_0e^{-\Sigma_j(1)} , \quad \alpha^{\pm}_j(x)=\alpha^{\pm}_0(x)e^{\mp\Sigma_j(x)} , \quad (12)$$

where $\Sigma_j(x)=2\sum_{k=1}^{j}\omega_k x^k$.

For initial conditions we have $\rho_0=\rho(0)$ and $\tilde\gamma_0(x)=\tilde\mu_0(x)=\rho_0\sum_{r\ge1}x^r=\rho_0x/(1-x)$ since the A and B initial distributions are random. This gives

$$\alpha^{+}_0(x)=\frac{1-(1-4\rho_0)x}{2(1-x)} , \quad \alpha^{-}_0(x)=\frac{1}{2} . \quad (13)$$

To complete the determination of the SSA model in term of initial data we specify now the stage factor ω_j. Since $2\tilde\mu(x,z)=\alpha^{+}(x,z)-\alpha^{-}(x,z)$, we have at the end of the stage j

$$2\Sigma_j(x)=\ln[2\alpha^{+}_0(x)]-\ln[1+4\tilde\mu_j(x)e^{-\Sigma_j(x)}]$$

when the solutions (12) and (13) are used. On the other hand, from Eq. (10), $\tilde\mu_j(x)=O(x^{j+1})$ and the previous relation reads

$$\sum_{k=1}^{j}\omega_k x^k=\frac{1}{4}\ln\left\{\frac{1-(1-4\rho_0)x}{1-x}\right\}+O(x^{j+1}) ,$$

which implies that

$$\omega_k=\frac{1-(1-4\rho_0)^k}{4k} , \quad k\ge1 . \quad (14)$$

The dynamics of the SSA model, i.e., its behavior as j increases, is thus exactly solved. For the density, it is convenient to write

$$2\Sigma_j(1)=\int_{1-4\rho_0}^{1}du\frac{1-u^j}{1-u}$$
$$=\int_0^{4\rho_0 j}\frac{dv}{v}\{1-e^{j\ln[1-(v/j)]}\}\ ,$$

which gives its continuation to any real positive j and its j behavior as $j\to\infty$,

$$\rho_j\sim\frac{e^{-\gamma/2}}{2}\left[\frac{\rho_0}{j}\right]^{1/2} \tag{15}$$

where $\gamma=0.577\,215\ldots$ is the Euler constant. It is in agreement with (3), according to our identification

$$\rho(t)=\rho_j\ ,\quad j=\xi(t)=r_0\ln(1+\omega_0 t)\ . \tag{16}$$

In order to check the validity of the mapping (16) between the SSA and the SA model, we have performed MC simulations of the SA process. These are done on 100 000 site lattices, filled with different densities, and statistical averages involve 100 histories, in order to reach large time (up to $\xi=300$) with good precision, the relative errors being 0.001 and 0.01 for the density and the correlations, respectively. In Fig. 1 we give a set of three typical examples. Two cases correspond to the same initial density $\rho(0)=0.25$ in order to illustrate the role of r_0, which changes from $r_0=1$ to $r_0=10$, the remaining case corresponding to $r_0=1$ with a different initial density $\rho(0)=0.10$. One can estimate on this figure the range of validity of the mapping (16): it gives the correct asymptotic behavior in all cases, and a good fit of the data at any time when r_0 is not too high.

On can also check the agreement between the pair correlations $X(r,t)$ and $Y(r,t)$ as defined in (1), and the corresponding quantities in the SSA model. One finds

$$X(r,t)=(A_r^+ + A_r^-)/2\rho_j\ ,$$
$$Y(r,t)=(A_r^+ - A_r^-)/2\rho_j\ , \tag{17}$$

where the $A_r^{\pm}$ coefficients are given by the expansion $\alpha_j^{\pm}(x)=\sum_{r\geq 0}A_r^{\pm}x^r$ and where j and ρ_j are given by (16). One checks in particular that $A_r^+=A_r^-$ if $0\leq r<j$, which implements $Y(r,t)=0$ if $0\leq r<\xi(t)$ as given by (4). It is also possible to consider the asymptotic regime where j and r go to infinity with R fixed, $r=Rj$, and to demonstrate that the correlations have in this limit nontrivial limiting functions $X_\infty(R)$ and $Y_\infty(R)$. We just quote our simplest result, corresponding to the initial value $\rho_0=\frac{1}{4}$, where $2\alpha^-(x)=\exp[\frac{1}{2}\sum_{k=1}^{j}(x^k/k)]$. Then $A_r^+=A_r^-=\Gamma(r+\frac{1}{2})/2\sqrt{\pi}\Gamma(r+1)$ for $0\leq r\leq j$ and thus $X_\infty(R)=\lim(2A_r^+/\rho_j)=2e^{\gamma/2}/\sqrt{\pi R}$ for $0<R\leq 1$. The functions $X_\infty(R)$ and $Y_\infty(R)$ are more generally defined piecewise on intervals $\Delta R=1$, and it appears that their R infinite limit 1 is practically reached at $R=2$. For $R\leq 2$ one finds

$$X_\infty(R)=2e^{\gamma/2}/\sqrt{\pi R}\ ,\quad 0<R\leq 2\ ,$$
$$Y_\infty(R)=\begin{cases}0\ , & 0<R\leq 1\\ X_\infty(R)\ln(\sqrt{R}+\sqrt{R-1})\ , & 1\leq R\leq 2\ .\end{cases} \tag{18}$$

In Fig. 2 we show the MC measured correlations $X(r,t)$ and $Y(r,t)$ of the SA process with $\rho(0)=0.25$, $r_0=1$. They are displayed in the scaled variable $R=r/\xi(t)$ for various values of the reaction radius $\xi(t)$. The asymptotic regime, practically reached for $\xi(t)\simeq 50$, is in perfect agreement with the prediction (18). In this example, where $r_0=1$, the correlations are in fact described at any time in terms of the SSA model [expression (17)].

In this work we have considered a static staggered annihilation model which can be solved in one dimension due to its screening property. The exact summation of

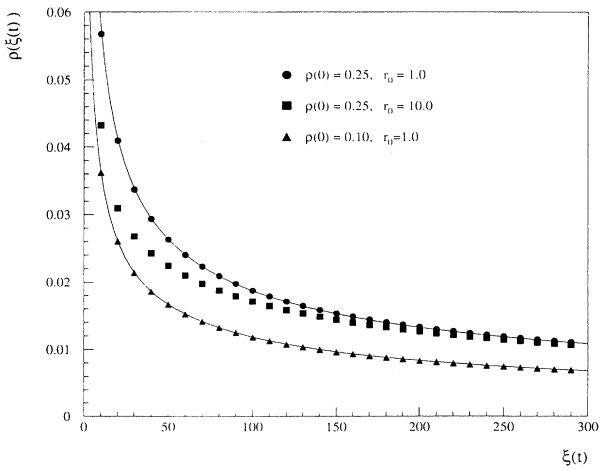

FIG. 1. The density for the static annihilation model given as a function of the reaction radius for various initial conditions. Dots represent MC data with errors smaller than the symbols. The curves are the SSA model predictions made using the mapping (16).

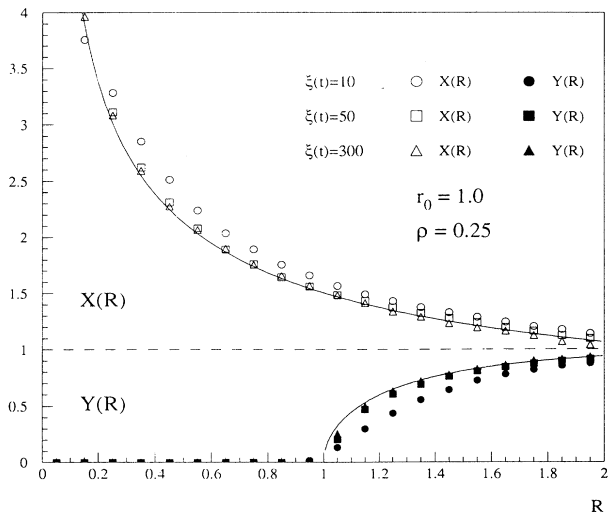

FIG. 2. The pair correlation functions $X(r,t)$ and $Y(r,t)$ given as functions of the scaled variable $R=r/\xi(t)$ for various values of the reaction radius $\xi(t)$. Dots are MC simulations of the static annihilation process with $\rho(0)=\frac{1}{4}$, $r_0=1$. Errors are smaller than the symbols. The curves are the asymptotic values (18) predicted by the SSA model.

the fluctuations at any scale implies a nontrivial behavior for the density and the correlations. Heuristic arguments on the reaction radius and MC experiments indicate that the static annihilation process, where the pair interaction is due to tunneling, behaves like the SSA model in the large-time regime. This clarifies the segregation mechanism and the role of the Kirkwood superposition law, which appears as a consequence of the screening property of the underlying SSA model. The solvability of the SSA model at any stage can be compared to other processes where the infinite hierarchy of equations coupling correlations is compatible with their factorization into products of basic distributions. This is the case for the trapping reaction $A+T\rightarrow T$ with immobile reactants and traps [12], and for ballistic annihilation in a one-dimensional fluid [13]. As a final remark, we want to stress that the "universality class" of the SSA model, from the asymptotic properties point of view, is probably not restricted to exponential tunneling laws.

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[1] V. Kuzovkov and E. Kotomin, Rep. Prog. Phys. **51**, 1479 (1988).
[2] D. C. Torney and H. M. McConnel, J. Chem. Phys. **87**, 1941 (1983).
[3] A. A. Lusknikov, Phys. Lett. A **120**, 135 (1987).
[4] J. L. Spouge, Phys. Rev. Lett. **60**, 871 (1988).
[5] C. R. Doering and D. Ben-Avraham, Phys. Rev. A **38**, 3035 (1988).
[6] G. H. Weiss, R. Kopelman, and S. Havlin, Phys. Rev. A **39**, 466 (1989).
[7] B. J. West, R. Kopelman, and K. Lindenberg, J. Stat. Phys. **54**, 1429 (1989).
[8] I. Peschel, V. Rittenberg, and U. Schultze, Nucl. Phys. B **430**, 633 (1994).
[9] H. Schnörer, V. Kuzovkov, and A. Blumen, Phys. Rev. Lett. **63**, 805 (1989); J. Chem. Phys. **92**, 2310 (1990).
[10] R. Brown and N. A. Efremov, Chem. Phys. **155**, 357 (1991).
[11] B. Bonnier, R. Brown, and E. Pommiers, Bordeaux Report No. CPTMB/PT/95-3, 1995 (unpublished).
[12] W. S. Sheu and K. Lindenberg, Phys. Rev. A **42**, 5025 (1990); P. L. Krapivsky, Chem. Phys. **168**, 15 (1992).
[13] J. Piasecki, Phys. Rev. E **51**, 5535 (1995); M. Droz, P. A. Rey, L. Frachebourg, and J. Piasecki, *ibid.* **51**, 5541 (1995).