Spatial Organization in the Two-Species Annihilation Reaction $A+B \rightarrow 0$

F. Leyvraz[1] and S. Redner[2]

[1]*Instituto de Fisica, Laboratorio de Cuernavaca, Universidad Nacional Autónoma de México, Cuernavaca, Mexico*
[2]*Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215*
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New features of the domain structure in the two-species annihilation reaction, $A+B \rightarrow 0$, are reported. A simple scaling argument predicts that the gaps between domains grows as t^{ζ}, with $\zeta = \frac{3}{8}$ and $\frac{1}{3}$, respectively, in spatial dimension $d=1$ and 2. The average density profile in a single domain exhibits a power-law tail near the domain edge. This feature has surprising implications for the spatial correlations of same-species reactants.

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In the diffusion-limited two-species annihilation reaction, $A+B \rightarrow 0$, it is now widely appreciated that fluctuations in the initial distribution of reactants cause the system to organize into continuously growing single-species domains, when the spatial dimension is less than four.[1-4] In this Letter, we present evidence for several new and unexpectedly rich features of this spatial organization. A new length scale is needed to describe the "gaps" between domains,[5] and the moments of the nearest-neighbor distance distribution for like particles do not obey simple scaling.

We consider an idealized model in which two species, A and B, are initially distributed at random on a d-dimensional lattice. Reactants are allowed to hop to a randomly chosen nearest-neighbor site. If an attempted move is to a site occupied by a particle of the opposite species, then both particles are removed from the system, while if the move attempt is to a site occupied by a particle of the same species, then the move is rejected. This exclusion introduces correlations which become negligible in the limit of large times and low concentrations. After each move attempt, the time is incremented by the inverse of the number of particles.

For this model, it is well known[1-4,6] that the concentration of particles $c(t)$ is proportional to $t^{-d/4}$ for $d \leq 4$. This decay can be understood by noting that after a time t, all the $c(0)l^d$ particles within a region of linear dimension $l \sim \sqrt{t}$ have had a chance to interact. Consequently, the number of particles remaining within this region will be equal to the initial fluctuations in particle number, a quantity which is of order $[c(0)l^d]^{1/2}$. Therefore,

$$c(t) \propto [c(0)l^d]^{1/2}/l^d \propto t^{-d/4}. \tag{1}$$

Concomitantly, an initially homogeneous system "coarsens" into alternating A-rich and B-rich domains[1-4,7-9] of linear dimension proportional to $t^{1/2}$, while the typical interparticle spacing grows as $c(t)^{-1/d} \sim t^{1/4}$ (Fig. 1). This simple picture does not fully account for many interesting aspects of the spatial structure, however. As we shall show, the gaps between domains grow at a rate intermediate to the typical interparticle spacing and the domain size. Within a single domain, the density profile has a nontrivial spatial variation in which the concentration vanishes in a power-law fashion as the domain boundary is approached. This results in the positive-integer moments of the distribution of nearest-neighbor distances between like particles being dominated by the large spacings in the periphery of the domain, while fractional-order moments are controlled by the more closely spaced particles in the domain core.

To appreciate these features, we first determine the scaling of the interdomain gap size by giving an alternative derivation for the known one-dimensional decay law in terms of the gap size. We postulate that the gaps are of (unknown) length $l_{AB} \sim t^{\zeta}$, so that in a time interval $\Delta t \propto l_{AB}^2$ there will typically be a reaction in each gap. This leads to a change in concentration which is proportional to the inverse domain size. Hence

$$\frac{\Delta c}{\Delta t} \approx \frac{dc}{dt} \propto t^{-1/2-2\zeta}. \tag{2}$$

Thus in order for $c(t)$ to be proportional to $t^{-1/4}$, it is necessary that $\zeta = \frac{3}{8}$. Our numerical simulations yield estimates for ζ which are within 0.01 of this theoretical prediction.

This result can also be obtained by examining the density profile *within* a domain, an approach which also yields the scaling behavior for the moments of the nearest-neighbor distance distribution of like particles, $\langle l_{AB}^n \rangle$. For obtaining this profile, we rescale each domain

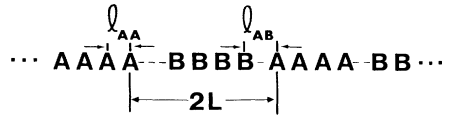

FIG. 1. Spatial distribution of reactants in one dimension illustrating the typical distance between neighboring particles of the same species, l_{AA}, the gap length (or nearest-neighbor distance between unlike species), l_{AB}, and the domain diameter, $2L$.

so that they all have the *same* length. Particles are placed at the closest integer point to the rescaled position, a prescription which introduces small truncation errors at early times. This rescaling is convenient, as it leads to a unique absorbing boundary condition for all domains. The particle densities of all the domains are superposed and the ordinate is then multiplied by a factor of $t^{1/4}$ in order to scale the data in one dimension [Fig. 2(a)]. As a function of the scaled abscissa, the scaled profile resembles a half-sine wave.

This shape can be understood in terms of a crude model in which the particles inside an A domain (for example) are diffusing independently within the region defined by the enclosing B domains whose edges are also viewed as moving diffusively. In a continuum approach, the concentration of A's thus obeys the diffusion equation

$$\frac{\partial c}{\partial t}=\frac{\partial^2 c}{\partial x^2}, \tag{3}$$

subject to the boundary conditions $c(\pm L(t),t)=0$, with the domain radius $L(t)$ increasing as $\sqrt{t}$. In the adiabatic approximation,[10] we thereby find

$$c(x,t)=\cos[\pi x/2L(t)]\exp\left[\text{const}\times\int_0^t dt'/L(t')^2\right], \tag{4}$$

in qualitative agreement with the shape of the distribution. We see that the concentration profile is the same as the case where the walls are stationary, and only the exponent of the power-law decay rate depends on the wall motion. This adiabatic approximation cannot be extended to the degree of accuracy necessary to find the exponent, however, due to the crudeness of our single-domain model.

For determining properties of the distribution of nearest-neighbor distances between same-species particles, the following aspects of the density profile are crucial. First, the density decays *linearly* to zero as the domain boundary is approached (Fig. 2). Second, the density profile can be roughly divided into a spatially uniform core and the linearly varying interfacial layer, with each region comprising a finite fraction of the domain length. From these observations, we postulate the following form for the scaled domain profile [Fig. 2(b)]:

$$\rho(z)\equiv c(x,t)t^{1/4}=\begin{cases}\rho_0, & |z|\le z^*,\\ \rho_0(1-|z|), & z^*<|z|<1-l_{AB}/L(t).\end{cases} \tag{5}$$

Here ρ_0 and z^* are constants, with z^* less than unity, and z is the scaled spatial coordinate, defined by $z=x/L(t)$. The upper limit for $|z|$ on the second line of Eq. (5) reflects the fact that there are no particles within a scaled distance of $l_{AB}/L(t)\sim t^{-1/8}$ from the domain edge.

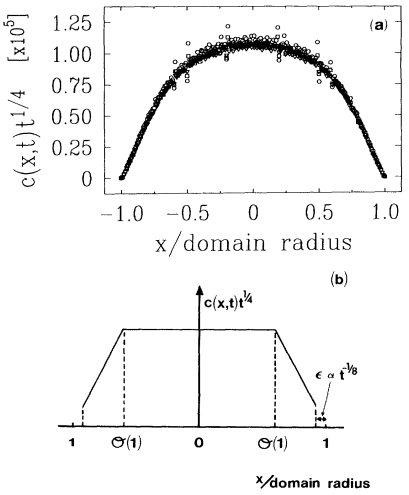

FIG. 2. (a) The scaled domain profile based on 64 realizations of a chain of 500000 sites with $c_A(0)=c_B(0)=0.4$. Shown are data for $t=194$ (○), $t=1477$ (□), and $t=11222$ (▽). This plot suggests the trapezoidal profile (b).

In terms of this trapezoidal profile, we can now give an alternative argument for the time dependence of the typical gap size l_{AB}. This distance is defined by the condition

$$\int_{-L(t)}^{-L(t)+l_{AB}} c(x,t)\,dx=1, \tag{6}$$

which merely states that of the order of one particle is within the gap. Using $c(x,t)\sim(L+x)/t^{3/4}$ appropriate for x close to $-L(t)$ [cf. Eq. (5)], the result $l_{AB}\sim t^{3/8}$ immediately follows.

We can also determine the time dependence of the moments of the distance distribution between adjacent same-species particles, $\langle l_{AA}^n\rangle$. According to the trapezoidal form, the reduced moments, $M_n\equiv\langle l_{AA}^n\rangle^{1/n}$, are

$$M_n\approx t^{1/4}\left[2\int_0^{z^*}\frac{dz}{\rho_0^n}+2\int_{z^*}^{1-\epsilon}\frac{dz}{\rho_0^n(1-z)^n}\right]^{1/n}. \tag{7}$$

Here $\epsilon\equiv l_{AB}/L(t)\propto t^{-1/8}$ is the aforementioned cutoff that specifies the location of the outermost particle in the domain in scaled units. Performing this integral yields

$$M_n\sim\begin{cases}t^{1/4}, & n<1,\\ t^{1/4}\ln t, & n=1,\\ t^{(3n-1)/8n}, & n>1.\end{cases} \tag{8}$$

Thus, as a consequence of the interfacial region, there is a logarithmic factor in the ratio between the average and typical distance between nearest-neighbor particles of the same species, and a power-law diverging factor for the higher moments. As $n\to\infty$, the reduced moment is dominated by the sparsely populated region near the periphery of the domain where nearest-neighbor particles are separated by a distance that grows as $t^{3/8}$.

These findings are corroborated by simulations. For various $n>1$, double-logarithmic plots of M_n vs t yield

straight lines of different slopes with exponent values that are in good agreement with Eq. (8). For $n < 1$, the M_n appear to approach a common limit, asymptotically, as we also expect. The slopes of the straight lines that pass through successive pairs of data points roughly extrapolate to exponent values of 0.26–0.27. Finally, for $n = 1$, the successive slopes are systematically increasing with time and extrapolate to an exponent value of about 0.29. The gradual increase of the exponent is not in accord with a logarithmic correction, although the value of the apparent exponent is in the range that is expected when a quantity which varies as $t^{1/4}\ln t$ is fitted with a simple power law. We do not fully understand the source of these various small discrepancies with Eq. (8).

We now determine the distribution of distances between neighboring same-species particles from the domain profile. Under the assumption that particles are distributed approximately at random according to the local density $c(x,t)$, then the probability of finding a nearest-neighbor distance between particles of the same species equal to s at spatial location x is

$$P_{AA}(s,x,t) = c(x,t)e^{-sc(x,t)}. \tag{9}$$

The average probability of finding a spacing equal to s is obtained by integrating over a domain and dividing its length. In terms of the scaled coordinate $z \propto x/t^{1/2}$ and the scaled density $\rho(z) \propto c(x,t)t^{1/4}$, this integral is

$$P_{AA}(s,t) \propto t^{-1/4}\int_0^{1-\epsilon} dz\,\rho(z)e^{-st^{-1/4}\rho(z)}. \tag{10}$$

Introducing the scaled spacing $\sigma \equiv s/t^{1/4}$, a saddle-point integration yields, for $\rho(z)$ vanishing linearly in z near the domain edge,

$$P_{AA}(\sigma) \propto F(\sigma)\exp(-\text{const}\times\sigma t^{-1/8}), \tag{11}$$

with $F(\sigma) \propto O(\sigma^{-2})$ as $\sigma \to \infty$. From this form, it is also possible to obtain the moments M_n already derived in Eq. (8). We expect to observe the power-law form for $F(\sigma)$ at a length scale intermediate to the typical and largest interparticle spacing, a range which unfortunately grows only as $t^{1/8}$. Thus the largest time in our one-dimensional simulation, $t = 11\,222$, does not appear to be long enough to yield good numerical evidence for this power law; however, the data clearly exhibit the asymptotic exponential decay (Fig. 3).

The above presentation can be extended to higher dimensions. In analogy with the one-dimensional case, we hypothesize that a domain in d dimensions has a core region of approximately constant density and a surrounding $(d-1)$-dimensional "skin" where the density vanishes as the domain edge is approached. Numerical simulations on a 1000×1000 square reveal a profile, obtained by superposing the one-dimensional profiles on each line of the square, which is qualitatively similar to the one-dimensional case, except for a more abrupt depletion at the domain edge.

To estimate the gap distance l_{AB}, we now assume that

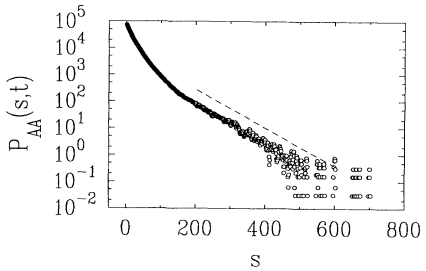

FIG. 3. Semilogarithmic plot of the smoothed distribution of nearest-neighbor distances for same-species particles $P_{AA}(s,t)$ at $t = 11\,222$. The slope of the best-fit straight line that fits the asymptotic decay (dashed and offset) vanishes as $t^{-3/8}$.

all the particles at the edge of the depletion zone are separated by a distance which scales as l_{AB}, leading to the number of boundary particles scaling as $(t^{1/2}/l_{AB})^{d-1}$. Then in a time interval which is proportional to l_{AB}^2, each of these boundary particles reacts, for $d \leq 2$, leading to a density change $\Delta c \sim (t^{1/2}/l_{AB})^{d-1}/t^{d/2}$. In analogy with Eq. (2), we find

$$dc/dt \sim t^{-1/2}l_{AB}^{-(d+1)}. \tag{12}$$

Matching the resulting solution with the known decay of $c(t) \sim t^{-d/4}$ for $d \leq 4$ yields $\zeta = (d+2)/4(d+1)$. Simulations in two dimensions give a value for ζ which is close to the predicted value of $\frac{1}{3}$. We expect that this dimension dependence for ζ holds in the range $1 \leq d \leq 2$. However, for $d > 2$, not every particle on the domain boundary reacts within any specified time interval, and we expect qualitatively different behavior, with a negligible depletion zone at the domain periphery.

In summary, the gap between domains is a new length scale, intermediate to the interparticle spacing and the domain size, in diffusion-limited two-species annihilation, $A + B \to 0$. The depletion of particles near the domain edge accounts for the multiscaling properties of the moments of the nearest-neighbor distance distribution for same-species particles, and also a more complete account for the spatial distribution of reactants in the system.

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