Escape and Finite-Size Scaling in Diffusion-Controlled Annihilation

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We study diffusion-controlled single-species annihilation with a finite number of particles. In this reaction-diffusion process, each particle undergoes ordinary diffusion, and when two particles meet, they annihilate. We focus on spatial dimensions $d > 2$ where a finite number of particles typically survive the annihilation process. Using scaling techniques we investigate the average number of surviving particles, M, as a function of the initial number of particles, N. In three dimensions, for instance, we find the scaling law $M \sim N^{1/3}$ in the asymptotic regime $N \gg 1$. We show that two time scales govern the reaction kinetics: the diffusion time scale, $T \sim N^{2/3}$, and the escape time scale, $\tau \sim N^{4/3}$. The vast majority of annihilation events occur on the diffusion time scale, while no annihilation events occur beyond the escape time scale.

Reaction-diffusion processes are found in most areas of science including biology, chemistry, physics, and geophysics [1–5]. Typically, in diffusion-controlled reactions, particles diffuse in space and a reaction occurs when two or more particles "meet" [6–9]. Being strongly interacting many-body systems, reaction-diffusion processes play a central role in pattern formation [10, 11] and in non-equilibrium statistical mechanics [12, 13].

Studies of simplified reaction schemes such as annihilation, coalescence, and aggregation show that there are two types of behavior. In sufficiently low spatial dimensions, significant spatial fluctuations develop and slow down the reaction kinetics [5, 6, 13–24]. This effect has been confirmed, both qualitatively and quantitatively, in a number of experiments [25–27]. In large spatial dimensions spatial fluctuations are minor, and the standard rate equation approach is applicable. The critical dimension which differentiates these two regimes of behavior depends on the reaction scheme [13].

The vast literature on non-equilibrium statistical mechanics of reacting systems is focused on spatially-homogeneous systems where the number of particles is infinite. Moreover, most of the theoretical methods used to describe reaction processes apply to spatially-homogeneous systems [17, 19, 21, 22, 24]. While there are a few exceptional studies of spatially-inhomogeneous [28, 29], or finite [30, 31] systems, little attention has been given to systems with a finite number of particles.

Here, we investigate diffusion-controlled reaction processes with a finite, yet large, number of particles in an unbounded space. We focus on the simplest possible reaction, single-species annihilation which is represented by the reaction scheme

$$A + A \to \emptyset\,. \tag{1}$$

In the annihilation process (1), identical particles, denoted by A, undergo Brownian motion and whenever two particles come into contact, they disappear. We focus on the initial condition where N particles occupy a $d-$dimensional ball (see Fig. 1). We also briefly discuss initial conditions where the occupied region has an intrinsic dimension smaller than d.

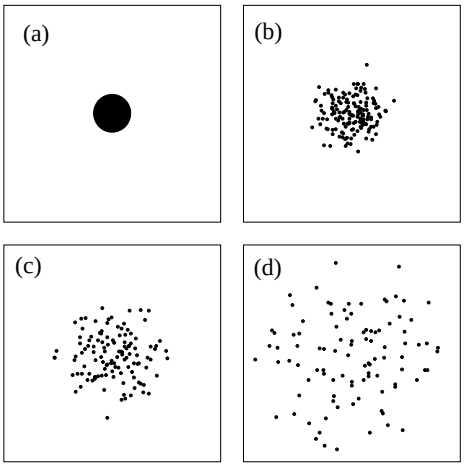

FIG. 1: Illustration of the diffusive escape process: (a) the initial condition with $N = 38,911$ particles inside a ball of radius $R = 21$ in three dimensions; (b), (c), & (d) show particle positions when 4.1%, 3.1%, and 2.5% of the initial particles remain. Particle positions are projected from three dimensions onto two dimensions.

We are especially interested in the ultimate fate of the system, that is, the behavior in the limit $t \to \infty$. This behavior follows from recurrence properties of a single random walk [13, 32]. A random walk on an ordinary lattice in dimension d is guaranteed to return to its starting site if and only if $d \leq 2$. Since the separation between a pair of particles also undergoes a random walk, the two particles are guaranteed to meet if and only if $d \leq 2$. Therefore in single-species annihilation, all particles disappear when $d \leq 2$, while a finite number *eternally* survive when $d > 2$ [33].

We focus on the interesting case $d > 2$, and we study the average number of surviving particles M as a function of the number of starting particles N. Our first result is the scaling law (see Fig. 2)

$$M \sim N^{\alpha} \qquad \text{with} \qquad \alpha = \frac{d-2}{d}, \tag{2}$$

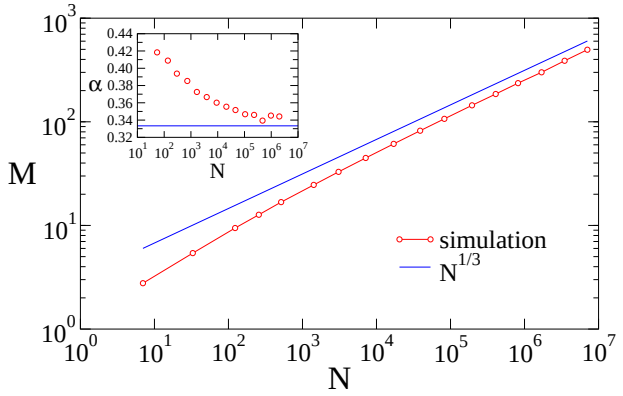

FIG. 2: The average number of surviving particles M versus the initial number of particles N. Initially, the particles occupy a ball on a three-dimensional lattice. The quantity M is measured by fitting the late-time behavior of $n(t)$ to the linear function $a+b\,t^{-1/2}$, as follows from (12). The inset shows the exponent $\alpha \equiv d\ln M/d\ln N$ versus N; the reference line $\alpha = 1/3$ is drawn as well.

which applies for $N \gg 1$. To derive (2), we study the time evolution of the number of particles. Our second result is that there are two time scales

$$T \sim N^{2/d} \quad \text{and} \quad \tau \sim N^{4/d}, \tag{3}$$

where T is the diffusion time, and τ is the escape time. The vast majority of annihilation events occur on the diffusion time scale, while no annihilation events events occur beyond the escape time scale.

The single-species annihilation process (1) can be realized either in continuous or in discrete space. In the continuous-space realization, particles have a finite size and undergo Brownian motion with diffusion coefficient D. In the discrete-space realization, particles reside in a d-dimensional hyper-cubic lattice. Each particle occupies a single site and hops with rate D to a neighboring site, chosen at random. When a particle hops onto an already occupied site, both particles disappear instantaneously. In the numerical simulations, we implemented the discrete-space version.

Our focus is the behavior of a finite number of particles. Hence, we consider initial conditions where a compact region of space is occupied by a finite number of particles, N, while its outer region is empty. We make two assumptions regarding the initial arrangement of the particles: (i) the occupied region is compact, and (ii) the particle density is uniform. Hence, the number of particles is proportional to the volume of the region: $N \sim L^d$, where L is the linear dimension of that domain. In the simulations, we implemented a uniform distribution inside a d-dimensional ball: all lattice sites within distance R of the origin are occupied.

The density $c(\mathbf{r},t)$ obeys the standard reaction-diffusion equation

$$\frac{\partial c}{\partial t} = D\,\nabla^2 c - K\,c^2\,. \tag{4}$$

In writing this equation, we assume that the particles are perfectly mixed, that is, particle positions are not correlated. Consequently, the reaction term is quadratic in the density. For single-species annihilation, the reaction equation (4) is valid in dimension $d > 2$. The reaction coefficient K scales with the diffusion coefficient D and the particle size a according to $K \sim Da^{d-2}$, as shown by Smoluchowski [7]. For the discrete-space realization, we identify D with the hopping rate, and a with the lattice spacing. Without loss of generality, we set $D = 1$, $a = 1$, and $K = 1$.

Using the reaction-diffusion equation (4) and a key simplifying assumption about the spatial arrangement of the particles, we can obtain a rate equation for the total number of particles at time t, $n(t) = \int d\mathbf{r}\, c(\mathbf{r},t)$. First, we integrate the reaction-diffusion equation (4) over the entire space and obtain

$$\frac{dn}{dt} = -\int d\mathbf{r}\, c^2. \tag{5}$$

This equation states that the rate of decline in the number of particles equals the total reaction rate.

In the initial state, particles are confined to a region of space with a *finite* volume. Importantly, the same remains true at all times. We expect that the particle "cloud" expands with time, but nevertheless, the size of this cloud remains finite because the number of particles is finite. Let us consider a cloud of particles, confined to within a region of volume V. In our heuristic analysis, we assume that the particles are uniformly distributed inside this region

$$c(\mathbf{r},t) = \frac{n}{V}\,, \tag{6}$$

while the density vanishes outside this domain, $c(\mathbf{r},t) = 0$. By substituting the uniform density (6) into the (5), we arrive at a rate equation for the average number of particles,

$$\frac{dn}{dt} = -\frac{n^2}{V}. \tag{7}$$

We reiterate that two assumptions were used to derive (7), viz. (i) the particles are confined to a finite region with volume V, and (ii) the particles are uniformly distributed inside this volume. But we made no assumptions about the shape of the confining region.

As the particles diffuse, the volume of the region confining them grows with time, $V \equiv V(t)$. Initially, particles are uniformly distributed and hence $V(t=0) \simeq N$. Particles that survive the annihilation process eventually manage to diffuse outside the initially occupied domain (see figure 1). From the diffusion length scale $\ell \sim t^{1/2}$, we deduce the growth $V(t) \sim \ell^d \sim t^{d/2}$. Therefore the confining volume exhibits two regimes of behavior,

$$V(t) \sim \begin{cases} N & t \ll T, \\ t^{d/2} & t \gg T. \end{cases} \tag{8}$$

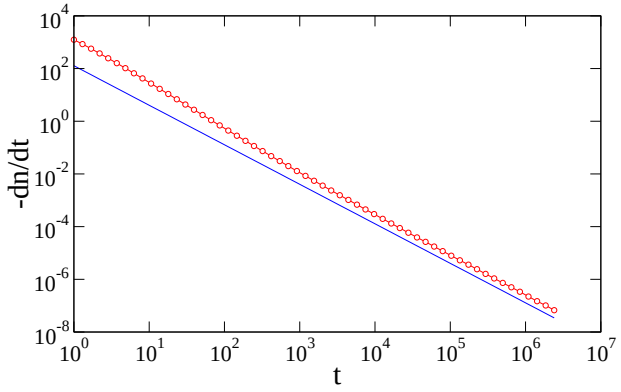

FIG. 3: The total reaction rate $-dn/dt$ versus time t for a system with $N = 7153$ particles in three dimensions. Also shown for reference is a line with slope $-3/2$.

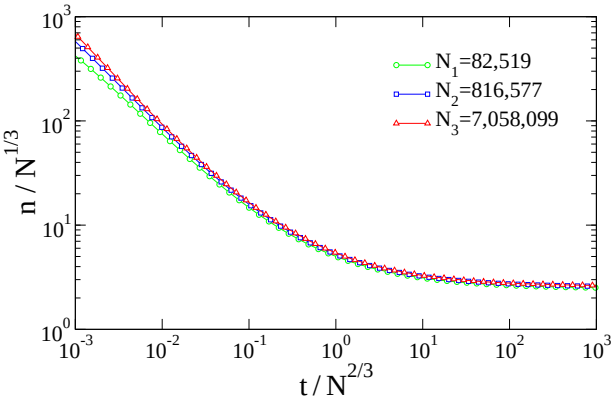

FIG. 4: The scaled number of particles $n(t)/N^{1/3}$ versus the scaled time $t/N^{2/3}$, for three different initial conditions. The particle numbers correspond to balls with radii $R_1 = 27$, $R_2 = 58$, and $R_3 = 119$. The simulation results represent an average over 10^3, 10^2, and 10^1 independent realizations.

The crossover time scale $T \sim N^{2/d}$ in (3) can be obtained by matching the two quantities. We term T the diffusion time, as this scale characterizes the time it takes a particle to diffuse outside the initially occupied domain. As we show below, this time scale separates two regimes of behavior: an initial regime during which most annihilation events occur, and a late regime during which the remaining few reaction events occur.

In the early regime, the reactions occur within the initially occupied region with volume $V \sim N$. Equation (7) becomes $dn/dt \sim -n^2/N$, and therefore,

$$n(t) \sim N\, t^{-1} \tag{9}$$

for $1 \ll t \ll T$. This rapid decay holds as long as most particles remain within the initially occupied domain.

We estimate the average number of particles that survive the first phase of the annihilation process by substituting the time scale T in (3) into Eq. (9) to yield

$$n(T) \sim N^{\alpha} \tag{10}$$

with $\alpha = (d-2)/d$. Since $n(T)/N \sim N^{-2/d}$, the vast majority of particles are annihilated at times $t \ll T$.

In the late regime, the confining volume grows according to $V \sim t^{d/2}$, and Eq. (7) becomes $dn/dt \sim -n^2/t^{d/2}$. By integrating this equation from t_0 till time t we find

$$\frac{1}{n(t)} - \frac{1}{n(t_0)} = \frac{1}{t_0^{d/2-1}} - \frac{1}{t^{d/2-1}}\,, \tag{11}$$

for $t > t_0 \gg T$. In writing (11) we ignored numerical factors of order unity. Setting $t_0 \approx T$ and taking the limit $t \to \infty$ in Eq. (11), we arrive at our main result: the scaling law (2) for the average number of surviving particles, $M \equiv n(\infty)$, as a function of the total number of starting particles N. From extensive numerical simulations we estimate $\alpha = 0.34 \pm 0.02$ for the exponent governing the scaling law (2) in three dimensions (Fig. 2). The reduction in the number of particles in the second stage of the reaction process is moderate, $n(\infty) \sim n(T)$. Hence, the finite fraction of particles that survive past the diffusion time scale, escape annihilation. The exponent α in (2) vanishes in the limit $d \to 2$, consistent with the fact that no particles survive when $d \leq 2$. Also, a finite fraction of the particles survive, $M \sim N$, in the limit $d \to \infty$.

In summary, the total number of particles exhibits two regimes of behavior

$$\frac{n(t)}{M} \sim \begin{cases} (t/T)^{-1} & 1 \ll t \ll T; \\ 1 + \text{const.} \times (t/T)^{(2-d)/2} & T \ll t. \end{cases} \tag{12}$$

Our simulation results confirm the asymptotic behavior $dn/dt \sim t^{-d/2}$ when $t \gg T$ (see Fig. 3). We have used the asymptotic $n(t) \simeq n(\infty) + \text{const} \times t^{(2-d)/2}$ to estimate the final number of particles $M \equiv n(\infty)$. For a given N, we measure the late time behavior and fit the number of remaining particles $n(t)$ to a linear function of $t^{(2-d)/2}$. The intercept of this line yields M.

A useful way to express the time-dependent behavior (12) is through the finite-size scaling form [34, 35]

$$n(t) \simeq N^{\alpha}\, F\left(t/N^{2/d}\right). \tag{13}$$

This form reflects that, in properly scaled units, the statistics become independent of the number of particles in the large-N limit (see Fig. 4). The scaling function has two limiting behaviors

$$F(x) \sim \begin{cases} x^{-1} & x \ll 1; \\ 1 + \text{const.} \times x^{(2-d)/2} & x \gg 1. \end{cases} \tag{14}$$

Since the number of particles is finite, the time at which the final reaction event takes place is also finite. The final reaction reduces the number of particles by two, and hence, the time of the final reaction event τ can be estimated from $n(\tau) - n(\infty) = 2$. Rewriting (12) as $n(t) - n(\infty) \sim N^{2\alpha}\, t^{(2-d)/2}$ we obtain the "escape" time

scale $\tau \sim N^{4/d}$ in (3). This time scale also sets a length scale $\rho \sim \tau^{1/2} \sim N^{2/d}$ for the escape process. Particles that manage to diffuse a distance comparable to the escape length scale ρ survive forever. Note that the escape length scale grows quadratically with the linear dimension of the initial domain $\rho \sim L^2$.

To summarize, the diffusion time scale $T \sim N^{2/d}$ is the time it takes particles to diffuse outside the initially occupied domain, and nearly all annihilation events occur in this time window. The escape time $\tau \sim N^{4/d}$ is the time at which the reaction process stops. The universal relationship, $\tau \sim T^2$, connects these time scales.

We now estimate the average lifetime of an annihilated particle. Nearly all particles disappear in the first time regime, $t \ll T$. From the density decay (9), we get t^{-2} for the annihilation rate and therefore the average lifetime is $\langle t\rangle \sim \int^T dt\, t\, t^{-2}$. Using $T \sim N^{2/d}$, we obtain

$$\langle t\rangle \sim \ln N. \tag{15}$$

Hence, the lifetime of reacting particles is relatively short, growing only logarithmically with system size. This feature allows us to simulate a large number of particles. Our Monte Carlo simulations utilize $\mathcal{O}(N)$ memory but require a quadratic number of operations per surviving particle, per unit time. Thanks to (15), the overall complexity of our *brute-force* simulations is only $\mathcal{O}(N^2 \ln N)$.

We now mention several extensions of the above results. First, we consider the multi-particle annihilation process

$$\underbrace{A + A + \cdots + A}_{m} \to \emptyset, \tag{16}$$

which generalizes the binary reaction process (1) to an arbitrary number m of reacting particles. The basic rate equation (7) becomes $dn/dt = -n^m/V$. By generalizing the above analysis, we obtain

$$M \sim N^{(d-d_c)/d}, \qquad d_c = \tfrac{2}{m-1}. \tag{17}$$

This scaling behavior holds above the critical dimension, $d > d_c$; for $d \le d_c$, all particles disappear. The diffusion time remains $T \sim N^{2/d}$, but the escape time is m-dependent, $\tau \sim N^{(2m)/[d(m-1)]}$.

Thus far, we have implicitly assumed that the dimension of the initially-occupied region δ equals the spatial dimension d. We now consider the situation where $\delta < d$ [36]. For example, when particles initially occupy a two-dimensional disk in three dimensions then $\delta = 2$ and $d = 3$. In general, the number of particles scales with the linear dimension as follows $N \sim L^\delta$. To address this problem, we use an alternative, probabilistic, approach.

We demonstrate this approach for the case $d = \delta$. Initially, the particles occupy a compact domain of volume L^d and the typical distance between particles equals 1. At later times, the surviving particles still occupy the same domain of volume L^d, but the typical distance between neighboring particles grows to $\ell \gg 1$. We take a test particle, located in the bulk of the domain, and estimate its survival probability, assuming that all other particles survive. Around the test particle, we draw spheres of radius $n\ell$, with $n = 1, 2, \ldots, L/\ell$ and n^{d-1} particles on each spherical shell. For two Brownian particles separated by distance r, the probability that they never meet is $1 - r^{-(d-2)}$[37]. The product of such probabilities,

$$\prod_{\ell=1}^{L/\ell} \left(1 - \frac{1}{(n\ell)^{d-2}}\right)^{n^{d-1}}, \tag{18}$$

gives a lower bound for the survival probability. If this product is finite in the limit $N \to \infty$, then the survival probability is finite. The product is finite if and only if its logarithm is finite and hence,

$$\frac{1}{\ell^{d-2}} \sum_{\ell=1}^{L/\ell} n \sim \frac{L^2}{\ell^d} \sim 1\,. \tag{19}$$

Therefore, to guarantee that the survival probability is finite we must choose $\ell^d \sim L^2$, and using the number of surviving particles, $M \sim (L/\ell)^d$, we recover (2).

This probabilistic argument can be generalized to situations where the initially-occupied region has dimension δ. Replacing the power n^{d-1} in the product (18) with $n^{\delta-1}$, and repeating the steps above, yields the average number of surviving particles

$$M \sim \begin{cases} N^{(d-2)/\delta} & \Delta < 2, \\ N(\ln N)^{-1} & \Delta = 2, \\ N & \Delta > 2. \end{cases} \tag{20}$$

Here, $\Delta = d - \delta$ is the co-dimension. For example, for a two-dimensional disk in three dimensions we have $M \sim N^{1/2}$. In general, the co-dimension governs the behavior. A finite fraction of the particles eternally survive when the co-dimension is sufficiently large, $\Delta > 2$, while the number of surviving particles grows algebraically with N when the co-dimension is small, $\Delta < 2$. We mention that Eq. (20) can also be derived from the time-dependent density obtained in [36].

In summary, we studied reaction kinetics of single-species annihilation starting with a finite number of particle. Using the rate equation approach and heuristic arguments, we derived finite-size scaling properties of the time-dependent number of particles. Systems with a finite, yet large, number of particles exhibit universal behavior, once time and particle number are properly scaled. We have shown that when $d > 2$, a finite number of particles escape the reaction process. This number scales sub-linearly with the total number of particles. In addition to the diffusion time that characterizes the process, we also found a much larger time scale which characterizes the escape process.

We note that our initial conditions: a "droplet" containing a finite number of reactants is physically relevant. While we focused on spherical droplets in our simulations, we expect the same qualitative behaviors occurs

for other compact initial conditions, say for particles occupying a $d-$dimensional cube and even for non-compact initial conditions as long as all moments of the distribution function characterizing the distance to the origin are finite.

Our analysis provides scaling predictions for average quantities such as the average number of surviving particles. It would be interesting to investigate the distribution of the number of surviving particles. Given the finite-size scaling form (13), we expect that a universal distribution emerges when the number of particle is large. The shape of this distribution is an interesting topic for future studies. Of special interest is the probability $E_d(N)$ that all particles disappear. Using the probabilistic approach (18)–(19), we obtained the following estimate for this extinction probability: $\ln E_d(N) \sim -N^\alpha \ln N$.

The behavior of other reaction processes is another topic for further research. We expect that our scaling results hold for the closely-related coalescence process, $A + A \to A$. However, the aggregation process, $A_i + A_j \to A_{i+j}$, with mass-dependent diffusion coefficients, e.g. $D_k \sim k^{-\mu}$, appears to be more challenging. Another related problem is two-species annihilation, $A+B \to \emptyset$, where the critical dimension is $d_c = 4$ [14, 18]. The behavior above the critical dimension should coincide with (2), but the behavior below the critical dimension is intriguing. Recurrence properties of Brownian particles again imply that no particle eternally survive when $d \leq 2$. Scaling arguments, along the lines of those used in this study, suggest $M \sim N^{1/2}$ for all $2 < d < 4$. It would be interesting to investigate this problem using theoretical or computational methods.

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