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Large-scale simulations of diffusion-limited *n*-species annihilation

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We present results from computer simulations for diffusion-limited *n*-species annihilation, $A_i+A_j\rightarrow 0$ $(i,j=1,2,\ldots,n;i\neq j)$, on the line, for lattices comprising of up to 2^{28} sites, and where the process proceeds to completion (no further reactions possible), involving up to 10^{15} time steps. These enormous simulations are made possible by the renormalized reaction-cell method. Our results suggest that the concentration decay exponent for *n* species is $\alpha(n)=(n-1)/2n$ instead of $(2n-3)/(4n-4)$, as previously believed, and are in agreement with recent theoretical arguments of Deloubrière *et al.* We also propose an expression for Δ, the correction-to-scaling exponent for the concentration decay, defined by $c(t)\sim t^{-\alpha}(A+Bt^{-\Delta})$.

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I. INTRODUCTION

Diffusion-limited reactions have attracted much interest in recent years [1,2]. The kinetics of such systems is dominated by local fluctuations in the concentration of the reactants, thus posing a formidable problem that has not yet been solved: there exists no comprehensive theoretical approach for the analysis of diffusion-limited processes.

Few select models are amenable to exact analysis. These include one-species annihilation, $A+A\rightarrow 0$, and two-species annihilation $A+B\rightarrow 0$ (see Ref. [3], and references therein). In one dimension, the particle density for one-species annihilation decays as $c(t)\sim t^{-1/2}$, while for two-species annihilation (with equal initial concentrations and same diffusion constants for the two species) $c(t)\sim t^{-1/4}$. In either case, the result is strikingly different from the mean-field kinetics of the corresponding reaction-limited process, $c(t)\sim 1/t$. To bridge the gap between these disparate behaviors, ben-Avraham and Redner [4] proposed the *n-species annihilation* model, where particles belonging to the *n* species $A_1,A_2,\ldots,A_n$ diffuse on the line and react immediately upon encounter, according to the scheme

$$A_i+A_j\rightarrow 0, \quad i,j=1,2,\ldots,n, \quad i\neq j. \tag{1}$$

For $n=2$, we recover the two-species annihilation, while in the limit $n\rightarrow\infty$ encounters between like particles are improbable and the model is equivalent to the one-species annihilation. For intermediate values of *n*, one expects $c(t)\sim t^{-\alpha(n)}$.

In Ref. [4] it was proposed, following a heuristic scaling argument and treating fluctuations via the van Kampen Ω expansion [5], that $\alpha(n)=(2n-3)/(4n-4)$. This was supported by numerical simulations of lattices of typically 10^6 sites, and up to 10^6 time steps. (In one time step, all the particles in the system move one lattice spacing each, on an average.) Recently, we have conducted extensive numerical simulations [6] following the method of renormalized reaction cells (RRC) [7–9]. The systems involved are up to $2^{28}\approx 2.7\times 10^8$ sites long, and the processes were simulated to completion (until no further reactions are possible), for up to 10^{15} time steps. The new data lead us to the conjecture that $\alpha(n)=(n-1)/2n$ [6]. We also find a correction to the main decay mode, of the form $c(t)\sim t^{-\alpha(n)}(A+Bt^{-\Delta(n)})$, $\Delta(n)=1/2n$. The same results were found, independently (and unbeknownst to us), by Deloubrière *et al.* [10]. In their theoretical derivation, they consider a simplified version of the *n*-species annihilation, where domains of alternating species lose particles to reactions at one and the same rate in a synchronous fashion. The approximation is more than reasonable, yet it does not rigorously apply to the original model, and analysis of corrections is certainly beyond its scope. Moreover, the simulations in Ref. [10] are comparable in size to those in Ref. [4]. In what follows, we report the results of our large-scale simulations, which strongly support the conclusions of Ref. [10]. We also propose a scaling relation for the correction exponent Δ for the *n*-species annihilation, and possibly for other reaction models where particles segregate into distinct domains.

II. SCALING

As is well known, local fluctuations in the concentrations of the different species drive the kinetics of the *n*-species annihilation [2–4]. An initially random homogeneous distribution of the particles evolves into a continuously growing mosaic of domains of alternating surviving species. Two length scales characterize the emerging distribution and dominate the system: the interdomain distance—the distance between the last particle in a domain and the first particle in the domain next to it—$\ell_{\mathrm{AB}}(t)$, and the domain length, $\ell(t)$ [11]. These quantities grow with time as

$$\ell(t)\sim t^{\beta}, \quad \ell_{\mathrm{AB}}(t)\sim t^{\gamma}. \tag{2}$$

Once the domains form, reactions might take place only at the domain boundaries, and the particles have to diffuse across the domain gap ℓ_{AB} to react with other species. This takes a typical time of $\Delta t\sim \ell_{\mathrm{AB}}^2/D$, where *D* is the diffusion constant. The change in particle concentration during time Δt equals the total number of domain boundaries divided by the lattice size *L*; $\Delta c\sim -(L/\ell)/L=-1/\ell$. Thus,

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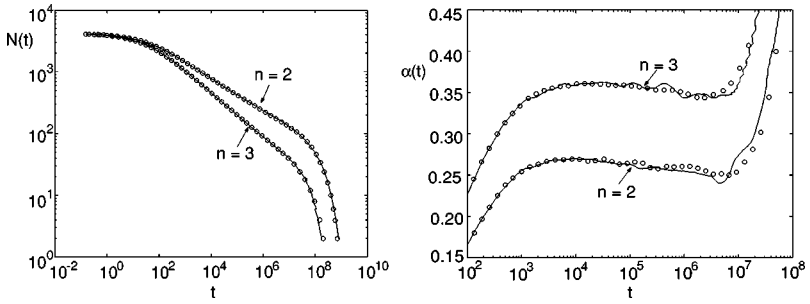

FIG. 1. Comparison between the traditional (circles) and RRC (solid line) simulation methods. Plotted are the number of surviving particles $N(t)$ (left) and the negative local slope $\alpha(t) = -d\ln N(t)/d\ln t$ (right) for 2^{16}-site lattices.

$$\frac{\Delta c}{\Delta t} \sim -\frac{D}{\ell \ell_{\mathrm{AB}}^2}. \tag{3}$$

On substituting relations (2) and $c(t) \sim t^{-\alpha}$, we derive the scaling rule

$$2\gamma + \beta - \alpha = 1. \tag{4}$$

Due to the underlying transport mechanism, we expect that domains grow diffusively, as $\ell \sim t^{1/2}$, so $\beta = 1/2$, and in effect there is only one independent exponent: $2\gamma - \alpha = 1/2$. The general scaling form holds also for the two-species annihilation in the presence of drift (and with hard-core repulsion between like species), where $\alpha = 1/3$, $\beta = 7/12$, and $\gamma = 3/8$ [9].

III. SIMULATION RESULTS

The n-species annihilation process is traditionally simulated as follows. The sites of a one-dimensional lattice are either empty or occupied by a particle (of one of the n species). Periodic boundary conditions are imposed, so the lattice is effectively a ring. At each Monte Carlo step, a particle is chosen randomly and is moved to the nearest site to its right or left with equal probabilities. If the target site is occupied by a particle of a different species, then both particles are removed from the system, mimicking reaction (1). If the target site is occupied by a particle of the same species, then the move is disallowed and it does not take place. Regardless of the outcome, time is incremented by $1/N(t)$, where $N(t)$ is the total number of extant particles.

As the simulation proceeds, the particle concentration declines and the typical distance between particles increases. The time spent on simulating the diffusive motion of the particles until they interact grows even faster, as the square of the distance between them. Because of that, computer simulations are limited to relatively short times. This problem is overcome by the RRC method [7–9].

In the RRC method, the particles occupy cells, rather than sites. Each time the concentration is halved, the cells are renormalized: every two cells are merged into one, and the time is renormalized accordingly. The typical time required to diffuse out of a renormalized cell twice as large as that of the previous generation is four times longer. Thus, physical time is simulated faster with each renormalization step and the process can be simulated to completion. Other details for the implementation of the RRC method are discussed in Ref. [9].

Simulations were performed on DEC Alpha processors running Linux. Since each lattice site requires six bytes (for species, number of particles, and a pointer to a list of populated sites that is used for fast selection at each Monte Carlo step), with 2 gigabytes (2^{31} bytes) memory we were able to simulate lattices comprising of up to 2^{28} sites. The compiler was given special #pragma pack(1) instructions to circumvent word alignment (which would allocate 32 bytes for our 6-byte site).

To test the technique, we have simulated the cases of $n = 2$ and $n = 3$ on lattices of $2^{16} = 65\,536$ sites, in both the RRC and the traditional simulation method. These lattices are small enough to enable the simulation of the process by the traditional method to completion. On the other hand, the system is large enough to let us examine the effect of the renormalizations: with 2^{16} sites and $c(0) = 1/16$ the RRC method requires 12 renormalizations. In Fig. 1(a), we compare the particle concentration as obtained by the two methods. In Fig. 1(b), we plot the negative of the local slope of the curves, the exponent $\alpha(t)$. The renormalizations are discernable only in this second, more stringent test, but the overall agreement is excellent. Similar results were obtained for the domain size and the distance between domains.

Having gained some confidence in the RRC method, we proceed to larger simulations. In Fig. 2, we show the surviving number of particles, $N(t)$, at time t, for $n = 3$, 4, and 5, and several lattice sizes. In Fig. 3, we plot the local decay exponent $\alpha(t)$ for our largest simulations of $n = 3$. The maximum of the curve at $t \approx 10^4$ agrees with the earlier simulations in Ref. [4], where a value somewhat smaller than the theoretical 3/8 had been reported. However, $\alpha(t)$ is seen to diminish with time, suggesting a long-time asymptotic

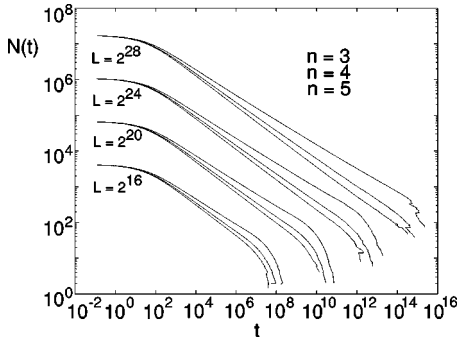

FIG. 2. Concentration decay for $n = 3$, 4, and 5-species annihilation. Plotted is the number of surviving particles, $N(t)$, for system sizes $L = 2^{16}$, 2^{20}, 2^{24}, and 2^{28} (bottom to top).

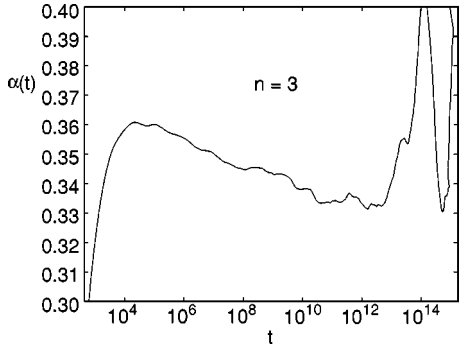

FIG. 3. Local decay exponent for three-species annihilation.

limit of $\alpha \approx 1/3$. This limiting value is confirmed in the data collapse (especially at long times) of Fig. 4, where we plot $t^{\alpha}c(t)$ vs t^{β}/L for various system sizes, and $\alpha=1/3$, $\beta=1/2$. Independent measurements show that $\beta=1/2$, as assumed, to within 2%, and the data collapse of Fig. 4 deteriorates with other choices for the values of α and β.

We have analyzed in this fashion $n=3$, 4, and 5-species annihilation, and measured the exponents α, β, and γ. Our results are summarized in Table I. In all cases, the scaling relation (4) seems to hold, and $\beta=1/2$ to within numerical errors. Looking for a simple expression of these results that would have the appropriate limits for the known cases of $n=2$ (two-species annihilation) and $n\to\infty$ (one-species annihilation), we were led to the conjecture [6]

$$\alpha=\frac{n-1}{2n}, \quad \beta=\frac{1}{2}, \quad \gamma=\frac{2n-1}{4n}, \tag{5}$$

a result derived independently by Deloubrière *et al.* [10]

Finally, let us address the issue of corrections to scaling of the concentration decay. We look for corrections of the form [12]

$$c(t)\sim t^{-\alpha}(A+Bt^{-\Delta}), \tag{6}$$

where A and B are constants. Our strategy consists of performing a least-squares linear fit of $A+Bt^{-\Delta}$ to $t^{\alpha}c(t)$, for different powers Δ, and searching for the value of Δ which minimizes the error. The expression (6) is expected to work

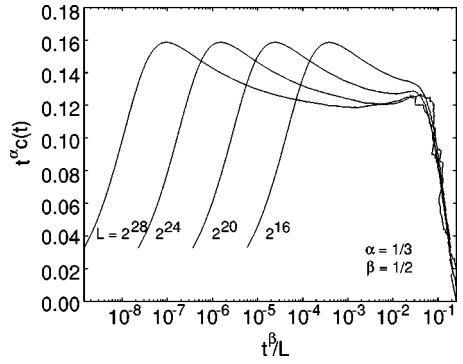

FIG. 4. Scaling of concentration, $c(t)=t^{-\alpha}\rho(t^{\beta}/L)$, for three-species annihilation. The best data collapse at late times is obtained for $\alpha=1/3$ and $\beta=1/2$ (shown).

TABLE I. Exponents α, β, and γ.

n	α	$\frac{n-1}{2n}$	β	γ	$\frac{2n-1}{4n}$
3	0.33(1)	0.333	0.50(1)	0.42(2)	0.417
4	0.39(2)	0.375	0.50(1)	0.44(1)	0.434
5	0.42(2)	0.400	0.50(1)	0.47(2)	0.450

only after the asymptotic regime sets in, and before finite-size effects begin, and the sticky part of our procedure decides which times demarcate this region. Experimenting with different choices gives us an idea about the errors involved. In Fig. 5, we show the best fits for the region $t=10^6$–10^{12} for $n=3$ on a $L=2^{28}$ lattice, where our data is most reliable. The results are most compatible with $\Delta=1/6$ [assuming $\alpha(3)=1/3$]. Similar tests for other values of n lead us to the conjecture that $\Delta(n)=1/2n$.

The correction exponent can be understood by a simple-minded argument. In deriving Eq. (3) we have assumed that the typical distance between reacting particles, at the edges of adjacent domains, is ℓ_{AB}. While this is correct, we note that, had the distribution of particles been homogeneous, the distance between reacting pairs would be typically $\ell_{AA}\sim L/c\sim t^{\alpha}$, quite different from the assumed $\ell_{\mathrm{AB}}\sim t^{\gamma}$. Using $\Delta t\sim \ell_{AA}^2/D$ in Eq. (3), instead of ℓ_{AB}^2/D, yields a faster decay; $c\sim t^{-(1-\beta)}$. Diffusion provides a natural drive toward a homogeneous distribution, and so it is conceivable that this faster mode of decay is manifested as a correction to the main behavior, $c\sim t^{-\alpha}$. It follows from Eq. (6) that the correction exponent is

$$\Delta=1-\beta-\alpha=\frac{1}{2n}, \tag{7}$$

where the last equality applies to the n-species annihilation, provided that the conjecture (5) holds. The more general relation works well for the two-species annihilation with drift, where $\alpha=1/3$, $\beta=7/12$, and $\Delta=1/12$ [9].

IV. SUMMARY AND DISCUSSION

We have presented large-scale simulation results for diffusion-limited n-species annihilation, in one dimension,

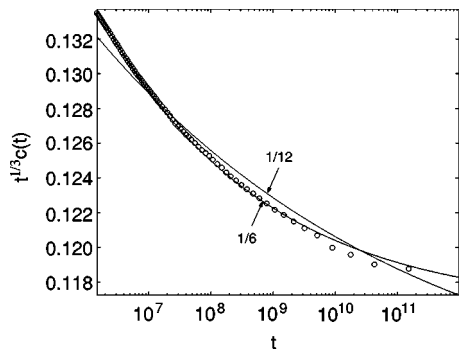

FIG. 5. Corrections to scaling. Simulation results (circles) are best fitted by Eq. (6), with $\Delta=1/6$ (solid line).

using the RRC method. Our simulations contradict previous work [4] and are in favor of new theoretical arguments advanced by Deloubrière *et al.* [10]. We have also provided an expression for the correction-to-scaling exponent Δ, valid for diffusion-limited reactions in one dimension, where the particles segregate into alternating domains. The corrections to the main decay mode are large, and explain the failure of Ref. [4] to obtain the correct asymptotic behavior with the size of simulations employed at that time. An important conclusion to be drawn is that predicting asymptotic behavior from the typical size of simulations used commonly in the field is dangerous. More advanced techniques and larger simulations seem to be imperative.

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