Anomalous Steady-State Properties of Long-Range A + A → 0 Reactions

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We study the steady-state properties of the long-range one-species reaction A + A → 0 in d-dimensional systems with an external random input of A particles. Particles are immobile and react via transfer rates dependent on the interparticle distance. For different forms of these transfer rates we calculate exactly, in form of bounds, the steady-state density of A particles. We show that they are described by the nonclassical dependence on the input rate and the parameters of the transfer rate. Our analytical results are in good agreement with experiments on excimer quenching and Monte Carlo simulation data.

1. Introduction

There has been much interest in the kinetics of one-species reactions, A + A → 0. Extensive studies (see, e.g., refs 1–9 and references therein) have led to a reasonably good understanding of the time evolution of this process, and a number of important results have been obtained. It was recognized[3-7,10] that for one-species reactions many-particle effects can be important, namely, the fluctuations in the number (odd or even) of particles in a certain volume. Depending on the dimensionally d of the system in which the reaction takes place, fluctuations either can lead to the renormalization of reaction constants or can dramatically change time dependences. Kinetic descriptions in terms of the conventional rate equation for the evolution of average density, $dC_A(t)dt = -KC_A^2(t)$, and their predictions that $C_A(t)$ decays asymptotically as $C_A(t) \propto 1/t$ do not hold for any spatial dimension d but only above some upper critical dimension d_c. Below d_c the fluctuations are relevant and leds to a slower decay[1-11]

$$C_A(t) \propto t^{-\nu}, \quad \nu < 1 \tag{1}$$

The values of d_c and ν depend on the reaction mechanism. Two distinct reaction mechanisms have been considered in the literature. The first is for direct energy-transfer problems[12] and concerns reactions involving immobile reactants with the rate of reaction (transfer rate) $W(r)$ being a function of the interparticle distance r, which decreases with the distance either algebraically

$$W(r) = \gamma(R_0/r)^n \tag{2}$$

where γ is the inverse lifetime decay rate and R_0 is the Forster radius, or exponentially

$$W(r) = \omega \exp(-\alpha r) \tag{3}$$

where α measures the range of interactions and ω is the amplitude of the transfer at the closest approach distance.

An algebraic dependence in eq 2 occurs for isotropic multipolar interactions. Here n equals 6 for dipole–dipole, 8 for dipole–quadrupole, and 10 for quadrupole–quadrupole interactions. An exponential dependence in eq 3 describes the case when the transfer is governed by exchange, e.g., for the triplet–triplet interactions between particles. We will refer to these mechanisms as long-range reactions (LRR) with multipolar transfer (MT) or exchange-mediated transfer (ET).

It was shown[7] that in systems with spatial dimensionality d less than n ($d_c = n$) the LRR kinetics in the case of multipolar transfer is described by eq 1 with $\nu = d/n$ and by the logarithmic dependence $C_A(t) \propto 1/\ln^d(t)$ for the exchange-mediated transfer ($d_c = \infty$). These long-time asymptotic forms were confirmed analytically,[8] observed experimentally,[13] and in numerical simulations.[14]

The second type of the reaction mechanism occurs in systems with mobile particles which react when they approach each other at a certain finite distance. It was proven[5-7] that the kinetics of one-species reactions involving diffusive particles [hereafter abbreviated as DLR (diffusion-limited reactions)] are correctly described by mean-field approximations based on the Smoluchowski approach, i.e., by the conventional rate equation with $K = K_{eff}$, where K_{eff} is the d-dimensional Smoluchowski "diffusive" constant. At large times the decrease of the averaged density follows $C_A(t) \propto 1/\int^t K_{eff}(t)\,dt$. The large-$t$ behavior of K_{eff} depends on the dimension of the system and, in general, on the dimension d_w of random walk paths executed by reactants. For regular diffusion $d_w = 2$. For several other types of random motion, e.g., when reactive species are attached to polymers[3,4,10,15] or execute random motion in disordered media or on fractal structures,[1-4,16,17] d_w can be larger than 2. In systems with $d > d_w$ the Smoluchowski constant approaches a constant value at infinite time. Thus, for $d > d_w$ the decrease of $C_A(t)$ follows the $1/t$ law. Conversely, for $d \leq d_w$ the interplay between fluctuation states and random migration of A particles results in a monotonic decrease[17] of K_{eff} with time, $K_{eff} \propto t^{-1+d_f/d_w}$ as $t \to \infty$ where d_f is the fractal dimension of the substrate. Consequently, the averaged density decays as[1,10,15,17] $C_A(t) \propto t^{-\nu}$ with $\nu = d_f/d_w$ for $d_f < d_w$. In the borderline case $d_f = d_w$ one has the logarithmic decrease of K_{eff} with time and $C_A(t) \propto \ln(t)/t$ (see, e.g., refs 5–9, 18, and 19).

These results can also be recovered by a simple approach[4,10,17,20]

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based on an analysis of fluctuation effects. Consider a system with spatial dimension d_f (d_f is an integer for Euclidean systems and noninteger for fractals) with particles which react instantaneously, A + A → 0, and perform a random walk with mean-square displacement $\langle X^2 \rangle \propto t^{2/d_w}$. Consider a region of the system of linear size l. After a time $t \propto l^{d_w}$ one can expect a complete mixing of particles in this region due to random motion. Therefore, all the particles have had a change to react, and there will be one particle left in this region if the initial number was odd and no particles if the initial number was even. Such a behavior will occur in every region of this size, and the particle density can be estimated as $C_A(t) \propto 1/l^{d_f} \propto 1/t^{d_f/d_w}$.

A decade ago the steady-state properties of the one-species DLR in systems with an external steady input of the reactive particles attracted considerable attention. It was recognized[1,2,16,17] that the same type of many-particle effects which dominates the kinetics of one-species reactions influences the steady-state properties. Consequently, the formal kinetic scheme

$$dC_A(t)/dt = -KC_A^2(t) + I$$

where I is the mean input rate, and its prediction that $C_A(t)$ exponentially fast approaches the steady-state density $C_A(\infty)$, which depends on I as

$$C_A(\infty) \propto I^{1/2}$$

holds only above the upper critical dimension d_c. Below d_c the dependence of $C_A(\infty)$ on I is given by[1,2,11,16,17]

$$C_A(\infty) \propto I^{\mu}, \quad \mu < {}^1/_2 \tag{4}$$

In particular, it was predicted that the steady-state density of particles in the DLR case depends on the mean input rate like eq 4 with $\mu = {}^1/_3$ for $d = 1$. Racz[11] has confirmed $\mu = {}^1/_3$ by rigorous calculations employing the analogy between diffusion-limited A + A → 0 reaction in 1D and the Glauber dynamics of a 1D Ising chain. By scaling arguments it was conjectured[11] that in the DLR case the static μ and the dynamic ν exponents are not independent and are related to each other by $\mu = \nu/(1 + \nu)$. Recent numerical and analytical investigations of DLR taking place on fractals suggest that $\mu = d_f/(d_f + d_w)$, in accord with Racz's conjecture. In systems with $d_f = d_w$ one has logarithmic corrections[2] to the mean-field predictions.

These results can also be obtained from the simple analysis[17] of fluctuations. Let us consider the balance between the production and annihilation of particles in some region in the system. The density of A particles in this region of linear size l, where l contains one particle on average, is governed by

$$l^{d_f} \frac{dC_A(t)}{dt} \propto Il^{d_f} - l^{-d_w}$$

where the first term describes the production of particles, I being the mean input rate, and the second describes the escape from the region due to random motion. In a steady state the region's size l depends on I as $l \propto I^{-1/(d_f+d_w)}$ and thus, the steady-state density follows $C_A(\infty) \propto 1/l^{d_f} \propto I^{\mu}$ with $\mu = d_f/(d_f + d_w)$.

For long-range one-species reactions theoretical analysis of the steady-state properties is still lacking. However, there is experimental evidence[13] for the appearance of an anomalous steady state in LRR in experimental measurements of the fluorescence yield in three-dimensional pyrene crystals with external steady pumping of excited states (excimers). At sufficiently high temperatures, when the excimers are diffusive, it was found that the steady-state density follows $C_A(\infty) \propto I^{1/2}$, in accord the DLR mechanism. In this case $d_w = 2$ and $d_f = 3$ so that normal behavior is expected. However, at low temperatures, when diffusion is suppressed and excimers decay by long-range dipole–dipole interactions, it was observed that for a wide range of input rates the steady-state density of excimers follows $C_A(\infty) \propto I^{1/3}$.

In this paper we examine the steady-state properties of the LRR in d-dimensional systems with an external steady input of A particles. We devise an analytical approach which allows us to find the averaged steady-state density of A particles, $C_A(I)$—as a function of the mean input rate exactly—in form of bounds

$$A_d f(I) \le C_A(I) \le B_d f(I)$$

where the prefactors A_d and B_d depend on d and n; and the dependence on the input rate, given by $f(I)$, is the same in the lower and the upper bounds. We show that $f(I)$ exhibits a mean-field type behavior, i.e., $f(I) \propto I^{1/2}$, only in the ET case with high rates I. For the MT case with arbitrary values of input rates $f(I)$ is given by

$$f(I) = \left(\frac{I}{\gamma R_0^{\,n}}\right)^{\mu}, \quad \mu = \frac{d}{d+n}$$

For the ET case with low input rates we find

$$f(I) = \left(\frac{\alpha}{\ln(\omega\alpha/I)}\right)^{d}$$

In the particular case $n = 6$ and $d = 3$ we obtain for μ exactly ${}^1/_3$ as in ref 13. Our values of the numerical factors A_d and B_d are also consistent with the experimental data, $C_A(I) = 0.205(I/\gamma R_0^6)^{1/3}$, presented in ref 13. The prefactors A_d and B_d in this case are 0.16 and 0.39, respectively.

We have checked our results by numerical simulations in $d = 1$ and $d = 2$ systems with multipolar transfer rates at different values of the parameter n and also found a good agreement between our analysis and simulation. We also found that the scaling relation between the dynamic and the static exponents, conjectured[11] for DLR, turns out to be valid in our case of long-range one-species reactions involving immobile species, suggesting that this relation might be universal for the processes of A + A → 0 type.

2. The Model

Consider a d-dimensional system with an external source producing particles randomly in time and space with a mean rate

$$\langle I(r,t) \rangle = I$$

The brackets denote a volume average. The particles are immobile and react irreversibly, A + A → 0, via a distance-dependent transfer rate $W(r)$, given either by eq 3 or by eq 4. The particle density is described by the stochastic equation

$$dC_A(r,t)/dt = I(r,t) - C_A(r,t) \int_V dr_1\, W(r - r_1) C_A(r_1,t) \tag{5}$$

where the subscript V below the integral means the integration extends over the entire volume V of the system. As t tends to infinity, the system evolves to a steady state with the expected steady-state density $C_A(I) = \langle C_A(r,t\to\infty) \rangle$.

We are unable to solve eq 5 exactly and resort to an approach somewhat similar to the estimates above. The general idea is to coarse grain the system into the macroscopic cells and to modify the transfer rate functions within each cell in order to make eq 5 tractable. We assume that if the transfer rate within each cell is enhanced compared to the original $W(r)$, effectively more particles will react and the steady-state density will be less than with the original $W(r)$, leading to a lower bound. Conversely, when we diminish the transfer rate effectively, fewer particles will react, and we obtain an upper bound on the steady-state density $C_A(I)$.

3. A Lower Bound

Suppose that we modify the original system as follows. First, let us divide the system into cells of a fixed linear size $2R$ which is to be determined. We introduce a new transfer rate, defined

as

$$W'(r) = \begin{cases} \infty, & r \le R \\ W(r) \text{ in eq 2 or 3}, & r > R \end{cases}$$

That is, we set the interactions between particles placed in one cell to be infinite, while the interactions between particles occupying different cells the same as in the original system. We neglect correlations between particles occupying different cells. Since the probability to find two particles close to each other in a homogeneous system would be smaller than that in the actual system, such an assumption can only increase the reaction rate and diminish the steady-state density and, hence, enhance the bound. Due to the infinitely large (instantaneous) transfer within the cell, there will be only one particle (occupied cell) if the initial number of particles in this cell was odd, and the cell will be empty if the number of particles was even. Correspondingly, if the source adds one particle to an empty cell, it will contain one particle, and if it adds a particle into an occupied cell, it becomes empty.

Let $P_1(i)$ be the probability of having one particle in the ith cell and $P_0(i)$ the probability to have the ith cell empty. For each cell, $P_1(i) + P_0(i) = 1$. The equation which governs the evolution of the ensemble average occupation probability $P_1 = \langle P_1(i) \rangle i$ reads

$$\frac{dP_1(t)}{dt} = IV_R(P_0 - P_1) - \frac{P_1^2}{V_R}\int_V dV\, W'(r) \qquad (6)$$

where V_R is the volume of the cell, $V_R = (2R)^d$. The first term on the rhs of eq 6 gives the balance between the creation of particles accounting for reaction, and the second term describes the loss of particles due to the intercell transfer.

For any values of parameters α and ω in the ET case and for $n > d$ in the MT case, the integral on the rhs of eq 6 exists, and eq 6 has the steady-state solution

$$P_1(R) = -Y(R) + \sqrt{Y(R) + Y^2(R)} \qquad (7)$$

$$Y(R) = \frac{IV_R^2}{\int_V dV\, W'(r)} \qquad (8)$$

The steady-state density of particles in the modified system, which we denote as $C_{low}(I,R)$, is

$$C_{low}(I,R) = P_1(R)/V_R \qquad (9)$$

Below we will analyze its behavior in the MT and ET cases.

Let us consider first the MT case. The function $Y(R)$ is given explicitly by

$$Y(R) = \frac{4^d(n-d)}{\Gamma_d}\frac{IR^{d+n}}{\gamma R_0^n}$$

where Γ_d is the surface area of a d-dimensional unit sphere.

To find the best lower bound on the steady-state density, let us analyze the behavior of $C_{low}(I,R)$ in eq 9 as a function of the trial parameter R. It is positive at any value of R and vanishes when R tends to zero or to infinity, i.e., $C_{low}(I,R)$ displays a nonmonotonic dependence on R (see Figure 1). When R equals R^*, given by

$$R^* = \left(\frac{\Gamma_d(n-d)}{d4^{d+1}n}\right)^{1/n+d}\left(\frac{\gamma R_0^n}{I}\right)^{1/n+d}$$

$C_{low}(I,R)$ approaches a maximal value, which we denote as $C_{low}(I)$. Evidently, $C_{low}(I)$ provides the best lower bound on the steady-state density in the original system. Explicitly,

$$C_{low}(I) = A_d\left(\frac{I}{\gamma R_0^n}\right)^{d/(d+n)} \qquad (10)$$

$$A_d = \left(\frac{n-d}{2^{d+1}n}\right)^{n/(n+d)}\left(\frac{2^{d+1}d}{\Gamma_d}\right)^{d/(n+d)} \qquad (11)$$

Therefore, in the MT case our lower bound on $C_A(I)$ predicts the dependence in eq 4 with $\mu = d/(d+n)$.

Consider next the case when the reaction between particles is mediated by exchange and $W(r)$ is given in eq 3. In this case $C_{low}(I,R)$ is defined by eqs 7 and 9 with the function $Y(R)$ equal to

$$Y(R) = \frac{2^{2d}I(\alpha R)^{2d}}{\Gamma_d \omega \alpha^d \eta(R)}$$

$$\eta(R) = \alpha^d \int_R^\infty dr\, r^{d-1} \exp(-\alpha r)$$

Taking the derivative of eq 9 with respect to R and setting it equal to zero, we obtain the maximum of the curve $C_{low}(I,R)$

$$\frac{d4^{d+1}I}{\Gamma_d \omega \alpha^d} = \frac{\exp(-2\alpha R^*)}{\eta(R^*)d + (\alpha R^*)^d \exp(-\alpha R^*)} \qquad (12)$$

A simple analysis shows that eq 12 does not necessarily have a solution, and consequently, $C_{low}(I,R)$ is nonmonotonic function of R only for some values of the mean input rate I. To see this, it is sufficient to note that the lhs of eq 12 can be arbitrarily large, depending on the value of I, while the rhs is a bounded function, which for any value of R^* is less than $1/\Gamma(d+1)$. Therefore, the solution of eq 12 exists only when the source intensity does not exceed the certain critical value

$$I_0 = \frac{\Gamma_d \omega \alpha^d}{d4^{d+1}\Gamma(d+1)}$$

For any value of I which exceeds I_0 the function $C_{low}(I,R)$ approaches its maximal value at $R = 0$. Therefore, at large input rates the best, i.e., the maximal lower bound is given by

$$C_{low}(I) = C_{low}(I,R=0)$$

which leads to the mean-field type dependence

$$C_{low}(I) = \left(\frac{1}{\Gamma_d \Gamma(d)}\right)^{1/2}\left(\frac{\alpha^d I}{\omega}\right)^{1/2} \qquad (13)$$

In the limit of small intensities, when $I \ll I_0$, we expect that the position $x^* = \alpha R^*$ of the maximum is large. In the limit $\alpha R^* \gg 1$ eq 12 simplifies to

$$\frac{G(d+1)I_0}{I} = (\alpha R^*)^d \exp(\alpha R^*)$$

and yields the following solution for the position of the maximum

$$R^* = \frac{1}{\alpha}\ln\left(\frac{\Gamma(d+1)I_0}{I}\right)$$

Consequently, for $I \ll I_0$ the lower bound on the steady-state density has an anomalous dependence

$$C_{low}(I) = \frac{\alpha^d}{2^{d+1}\ln^d(\Gamma(d+1)I_0/I)} \qquad (14)$$

4. An Upper Bound

To calculate an upper bound on the expected steady-state density, we again coarse grain the system into the cells of a trial linear size $2R$ and define a new transfer rate function $W''(r)$ given by

$$W''(r) = \begin{cases} W(r) \text{ in eq 2 or 3}, & r \le R \\ 0, & r > R \end{cases}$$

i.e., we diminish the rate of interactions within each cell assuming

that each pair of particles is separated by the maximal possible distance and completely ignore intercell transfer. The system modified in such a way evolves toward a steady-state particle density $C_{upp}(I,R)$. In this system more particles survive, and the steady-state density $C_{upp}(I,R)$ will exceed $C_A(I)$. Let us define $N(R,t) = C_{upp}(I,R)V_R$—the number of particles in a cell. The ensemble average $N(R,t)$ is given by

$$\frac{dN(R,t)}{dt} = IV_R - {}^1/_2 N(R,t)(N(R,t)-1)W(R) \quad (15)$$

where the first term describes the production of particles in a cell and the second one describes the loss of particles due to the reaction between them; $N(N-1)/2$ is the number of interacting pairs in the ensemble of N particles, and $W(R)$ equals either $\gamma(R_0/R)^n$ in the MT case or $\omega \exp(-\alpha R)$ in the case of exchange-mediated transfer.

The steady-state solution to eq 15 reads

$$N(R) = \frac{1}{2}\left[1 + \left(1 + \frac{8IV_R}{W(R)}\right)^{1/2}\right] \quad (16)$$

and the corresponding steady-state density is defined as

$$C_{upp}(I,R) = N(R)/V_R \quad (17)$$

In the MT case the steady state density $C_{upp}(I,R)$ defined by eq 17 takes the form

$$C_{upp}(I,R) = \frac{1}{2^{d+1}R^d}\left[1 + \left(1 + \frac{2^{d+3}IR^{d+n}}{\gamma R_0{}^n}\right)^{1/2}\right] \quad (18)$$

Again, we have a bound which is a nonmonotonic function of the trial parameter R (see Figure 1). It diverges as R^{-d} when R tends to zero and tends to infinity as $R^{(n-d)/2}$ for $R \to \infty$. At

$$R = R^* = \left(\frac{nd}{2^{d+1}(n-d)^2}\right)^{1/(n+d)}\left(\frac{\gamma R_0{}^n}{I}\right)^{1/(n+d)}$$

$C_{upp}(I,R)$ approaches a minimal value which we term as $C_{upp}(I)$. Evidently, this value provides the best upper bound to $C_A(I)$. Explicitly, in the MT case it can be written down as

$$C_{upp}(I) = B_d\left(\frac{I}{\gamma R_0{}^n}\right)^{d/(d+n)} \quad (19)$$

$$B_d = \frac{n^{n/(n+d)}}{(n-d)^{(n-d)/(n+d)}\,(2^n d)^{d/(n+d)}} \quad (20)$$

Therefore, in the MT case we have obtained the lower and upper bounds on the steady-state density which have essentially the same dependence on the dimensional parameters, i.e., γ, R_0, and I, and differ only by numerical prefactors. We have compared our predictions with the available experimental data, presented in ref 13. It was found[13] that in the $d = 3$ and $n = 6$ case the best fit for the experimental data is provided by the curve $C_A(I) = 0.205(I/\gamma R_0{}^6)^{1/3}$. The comparison of results is presented in Figure 1 and shows a good agreement between the analytical and experimentally observed values of prefactors.

Let us analyze next the behavior of an upper bound in the ET case. Here $C_{upp}(I,R)$, is

$$C_{upp}(I,R) = \frac{1}{2^{d+1}R^d}\left[1 + \left(1 + \frac{2^{d+3}IR^d \exp(\alpha R)}{\omega}\right)^{1/2}\right] \quad (21)$$

It is easy to see that $C_{upp}(I,R)$ in eq 21 displays a nonmonotonic behavior as a function of the parameter R at any value of the input rate. The position of the minimum is given implicitly by

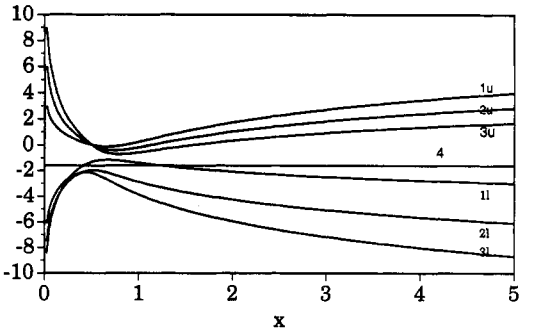

Figure 1. Multipolar transfer with dipole–dipole interactions, $n = 6$. Plot of the dimensionless functions $\ln(C_{low}(I,R)(\gamma R_0{}^n/I)^{d/(d+n)})$ (with $C_{low}(I,R)$ defined by eqs 7–9) and $\ln(C_{upp}(I,R)(\gamma R_0{}^n/I)^{d/(d+n)})$ (with $C_{upp}(I,R)$ from eq 18) vs the dimensionless variable $x = (I/\gamma R_0{}^n)^{1/(d+n)}R$. Lines 1u, 2u, and 3u are upper bounds for $d = 1$, 2, and 3, respectively, and lines 1l, 2l, and 3l are lower bounds. The solid line (4) is the fit of experimental data in ref 13, $\ln(C_A(I)(\gamma R_0{}^6/I)^{1/3}) = -\ln(115)/3$.

the equation

$$(\alpha R^*)^d(\alpha R^* - d)^2 \exp(\alpha R^*) = \frac{d\omega\alpha^d}{2^{d+1}I} \quad (22)$$

The asymptotic solution to eq 22 in the limits of small and large input rates is as follows. At large input rates, $I \gg d\omega\alpha^d/2^{d+1}$, the position of the minimum tends to a constant value

$$R^* = d/\alpha$$

Consequently, in this limit we recover mean-field type dependence

$$C_{upp}(I) = \frac{\exp(d/2)2^{(3-d)/2}}{d^{d/2}}\left(\frac{\alpha^d I}{\omega}\right)^{1/2} \quad (23)$$

which differs from the corresponding lower bound in eq 13 only by a larger value of the prefactor.

For the opposite limit, $I \ll d\omega\alpha^d/2^{d+1}$, we find a logarithmic dependence

$$R^* = \frac{1}{\alpha}\ln\left(\frac{d\omega\alpha^d}{2^{d+1}I}\right)$$

and thus obtain the upper bound on the averaged steady-state density

$$C_{upp}(I) = \frac{\alpha^d}{2^{d+1}\ln^d(d^2 2^{d+1}\Gamma(d+1)I_0/\Gamma_d I)} \quad (24)$$

5. Numerical Simulations

We have done Monte Carlo simulations in dimensions $d = 1$ and $d = 2$ with the long-range transfer rate in eq 3. This type of numerical calculation difficult when n is large because we test an effective rate law

$$I = K(n,d)C_A{}^X(I)$$

where the effective reaction order $X = (n+d)/d$ and the prefactor increase tremendously as function of n. Therefore, low densities require miniscule input intensities, I, and consequently, the time τ necessary to reach a steady state should be of the order of

$$\tau \propto \frac{C_A(I)}{I} \propto \frac{1}{K(n,d)C_A{}^{-n/d}}$$

which rapidly reaches the limits of normal computing power.

In Figure 2 we see an illustration of this. We display on a log–log scale results of our computer simulations for $n = 2$, 3, 4, 5, 6, and 7 in $d = 1$. These simulations are performed on a lattice with $N = 1000$ sites and cyclic boundary conditions. The random number generator was biased to take into account the discrete

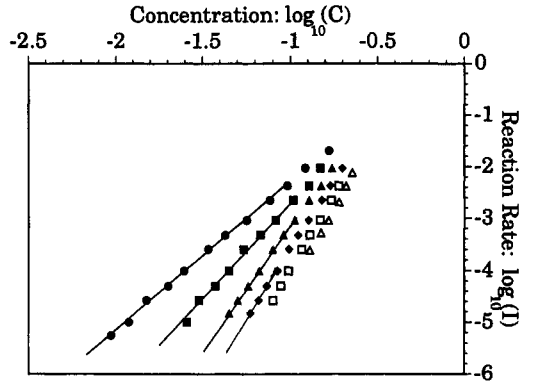

Figure 2. Rate laws on a log–log plot for $d = 1$. Symbols are Monte Carlo simulations. Black circles, squares, triangles, and diamonds denote the data for $n = 2$, 3, 4, and 5, respectively. Open squares and triangles correspond to the data for $n = 6$ and $n = 7$. Lines are the best power law fit computed for a density of $C_A < 0.1$.

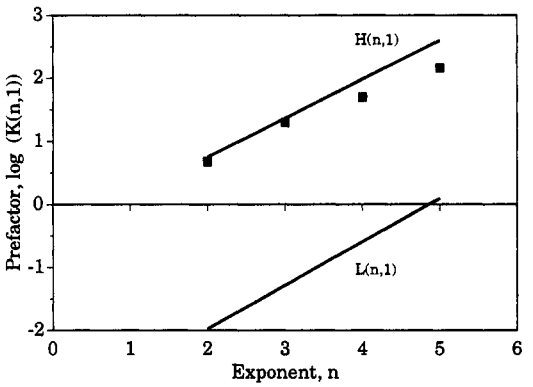

Figure 3. Slopes of the linear fit plotted as a function of n. The solid lines are the lower and upper bounds.

positions of the lattice. We made sure that all reaction probabilities (even for the shortest distances) precisely verify the scaling law with exponent n. We show as a dashed line the linear fit computed for densities $C_A < 0.1$ for $n = 2$, 3, 4, and 5. For $n > 5$ the fit could not be computed. When the computed slopes are compared with the theoretical predictions, the agreement is fair. Figure 3 shows the estimated prefactor $K(n,d)$ as a function of n on a log-normal scale. We also plotted the lower and upper bounds with (γR_0^n) found from the completeness relation, $2\sum_{k=1}^{n} k^n = 1/\gamma R_0^n$. The Monte Carlo values indeed fit between the bounds.

We also tested our theory for $d = 2$. Since the on-lattice simulation already posed nontrivial computational difficulties in $d = 1$, and these difficulties promised to increase at higher d, we performed an off-lattice simulation. At low densities there should be no difference between an on-lattice result and an off-lattice result. Off-lattice simulation allows us to rescale space and time to whatever regime is most convenient. Our simulations were done at constant intensity of one particle per Monte Carlo step, while γR_0^n was varied. However, a trivial rescaling of the time per Monte Carlo step will transform our parameters into ones of constant γR_0^n and varying I. Simulations were run in a square domain with periodic boundary conditions in which the size of the domain was varied to keep the total particle number roughly constant. Care was taken to ensure that the system reached the steady state before measuring density. Shown in Figure 4 are

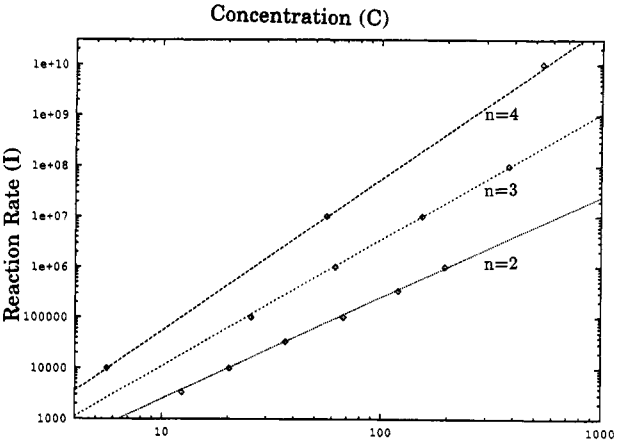

Figure 4. Rate laws on a log–log plot for $d = 2$ and $n = 2$–4. The power law fits are $25x^{2.0}$, $25x^{2.55}$, and $60x^{3.0}$.

plots of density versus input rate for $n = 2$, 3, 4. The power laws agree well with the scaling result $I \sim C^{1+d/n}$. The prefactors for $n = 3$, 4 fall within the upper and lower bounds derived above.

6. Conclusions

We have examined the steady-state density of immobile particles in systems with long-range one-species reactions and external random input. For different forms of reaction probability, we have obtained this density exactly, in form of bounds with the same dependence on the mean input rate but differ by numerical factors. This dependence is not consistent with mean-field predictions and stems from the many-particle effects—fluctuations of particle density in certain volumes. We have compared our results with experiment and numerical simulations and found that they are in good agreement.

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