Aging in two- and three-particle annihilation processes

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We investigate the global two-time density-density correlations of two- and three-particle annihilation processes. We show that the dynamical correlations scale with the ratio of the times, and thus exhibit aging. The phenomenon of aging in these processes can be understood in terms of a mean-first-passage-time approach to the motion of the system in phase space. We find that aging does not result from the spatial correlations and domain growth in the system, but from a particular slowing down of the dynamics as the global density decreases. This result holds also in one-dimensional diffusion-limited pair annihilation process, for which we calculate the exact scaling form of the autocorrelation function. [S1063-651X(98)09802-X]

PACS number(s): 05.40.+j, 82.20.Mj, 02.50.Ey

I. INTRODUCTION

Aging in glasses [1] and spin glasses [2,3] is now the focus of intense experimental [2,4] and theoretical [5–13] investigations. Typically we consider a system prepared in a nonequilibrium state at time $t=0$; it evolves for a duration of time t_w, and we call this the waiting time or the age of the system. Then we observe how a macroscopic property at time t_w+t is correlated to its value at t_w. Let us denote this correlation by $C(t_w,t_w+t)$. A stochastic process is said to be aging if this autocorrelation is a function of the ratio t/t_w of the two times. This is in contrast to stationary processes for which the autocorrelation function would be independent of t_w and depend only on the time difference t. Thus aging processes constitute a subclass of nonstationary processes. Physically, the dependence of correlations on the ratio of the times implies a scaling property: a young system and an old system evolve the same way if their evolution times are measured in units of their respective ages. One can find aging in a system that is either perennially in a nonequilibrium state, or that relaxes very slowly to its equilibrium state. In the former case one would usually find aging for all large waiting and relaxation times whereas in the latter one can detect aging on time scales that are large (so that transients die out) but not too large compared to the equilibration time. More importantly, for both classes of systems, aging would be present if the relaxation time from a quasiequilibrium state to the next increases with the time it takes to reach the quasi-equilibrium state: *The more you wait, the longer the system takes to relax.*

It is clear from the above discussion that glasses provide prototypical models for systems that exhibit aging, owing to the presence of energy [6] and/or entropy [13] barriers. It is also clear that the phenomenon of aging should indeed be present in a rather large class of slowly relaxing nonequilibrium processes. In this paper we consider reaction-diffusion systems of particles hopping and annihilating on a lattice. We are particularly interested in the two generic cases (i) where diffusion is sufficiently fast to erase spatial density correlations resulting from the annihilation process, and (ii) where diffusive mixing is inefficient and large fluctuations

persist. We show that under both circumstances the time correlations of the surviving number of particles exhibit aging scaling.

The paper is organized as follows. In the next section we describe the diffusion-limited annihilation processes we are investigating. Since we do not assume the reader to be familiar with such processes we provide a somewhat longer than usual introduction to the problem we want to address. We show that in the limit of large diffusion constant (or, equivalently, for strong repulsive forces between reactants) the problem can be mapped exactly onto a directed random walk on an integer lattice, with site-dependent transition rates. The random walk modeling of the process is discussed in Sec. III. We consider in Sec. IV the random walk process and derive the master equation for the first passage time densities. Employing generating function techniques we obtain exact expressions for the mean first passage time from an arbitrary lattice site to another. We then interpret the waiting and the relaxation times in terms of appropriate mean first passage times, and show that the former increases with the latter, signaling the presence of aging in these models. Mean-first-passage considerations help us to obtain also the time scale over which the phenomenon of aging occurs. In Sec. V, we obtain by exact numerical calculation the autocorrelation function of the random walk process and show that it scales as the ratio of the observation time to the waiting time, over the time scales derived from the mean-first-passage-time considerations. The principal conclusions are presented in the last section. In the Appendix we consider separately diffusion-limited pair annihilation in one dimension where, as opposed the models discussed in Secs. II–V, diffusive mixing is extremely weak. We show that also this process is aging and calculate analytically the exact scaling form of the autocorrelation function.

II. DIFFUSION-LIMITED ANNIHILATION PROCESSES

We consider processes of a single species of particles that diffuse and react on encounter, assuming that the reaction products play no role in the subsequent dynamics of the annihilation process. Processes of this kind, e.g., diffusion-

limited pair annihilation $2A \to \varnothing$ (DLPA), coagulation (or sometimes more appropriately called fusion) $2A \to A$ (DLC), three-particle annihilation $3A \to \varnothing$ (DL3A), etc. have a long history of study, an important ingredient being the theory of diffusion-limited reaction based on the work by Smoluchovsky [14]. Already at that time it was realized that a naive rate equation approach for the density loss—$\dot{\rho} = -\lambda \rho^k$ for the k-particle annihilation process with reaction rate λ—fails if diffusive mixing of reactants is too weak to destroy spatial particle density correlations. Such correlations, in fact, anti-correlations, build up because the annihilation process creates empty regions and thus particles are more likely to be found far apart rather than in close proximity. This effect is strong in low dimensions and decreases with increasing dimensionality of the system. Since the beginning of the 1980s this early insight, which is based on a fluctuation improved mean-field approach, has been confirmed and vastly extended by exact results on DLPA and DLC in one dimension, see [15] for a recent review. More recently, renormalization group studies have further clarified the role of the dimensionality of the system. This is briefly reviewed in [16]. We would like to mention in passing that it has been realized that DLPA and DLC are equivalent in the sense that the generators of their respective stochastic time evolution (see below) are related to each other by a similarity transformation [17]. Hence, in what follows we need to consider only DLPA for the case of two-particle annihilation processes.

For the purpose of this work it is important to note that the mean-field rate equation approach (which completely neglects all spatial correlations) provides an appropriate framework for DLPA in dimensions larger than two for two-particle annihilation and in dimension larger than one for the three-particle annihilation processes [18]. In higher-order particle annihilation processes the density fluctuations are irrelevant already in one dimension. We shall not consider such processes. Hence, for an investigation of the phenomenon of aging in these processes it is sufficient to examine the limiting cases of strong fluctuation effects (DLPA in one dimension with finite diffusion rate) and weak spatial density correlations, respectively (all diffusion-limited single-species annihilation processes in three dimensions or DLPA with infinite diffusion rate in one dimension).

Of course, within a pure mean-field framework there is no possibility of studying aging, which is a phenomenon observed by measuring temporal correlations. Hence we shall set up the problem as follows: we first formulate the full process of diffusion-limited annihilation in any dimension in terms of a master equation. Then, in order to account for the observation that correlations are weak in three dimensions we shall employ a technical trick to simulate this situation, but at the same time retain the temporal correlations of the total particle density. This is achieved by taking the limit of infinite diffusion rate, and at the same time leaving the effective reaction rate constant. As will be shown in Secs. IV and V, annihilation processes without spatial correlations *do* exhibit aging.

Note that this situation is a ''worst case scenario.'' If one could argue for the phenomenon of aging on the basis of the theory of diffusion-limited reactions, e.g., by using domain-size arguments [19], then the question would remain whether aging survives in the case of rapid diffusion, which surely speeds up the annihilation process. The answer to this problem is not obvious as the very presence of spatial correlations might conceivably be the origin of this supposed aging. Phrased differently, if one can establish aging for this limit of fast diffusion, then surely one expects it to occur in processes with relatively weak diffusive mixing where the dynamics is slower.

This simple argument is confirmed to be correct in a third step for DLPA in one dimension, where spatial correlations extend over regions of monotically increasing length $\xi \propto \sqrt{t}$ [20] and the decay of the particle density is anomalously slow [21]. We conclude that the origin of aging in this system does not stem from spatial correlations and increasing domain sizes, but from the increasingly slow relaxation of the uncorrelated annihilation process [22]. Since the nature of our treatment of the one-dimensional problem is very different from the main course of our investigation and, also, since our result is not at all surprising, this calculation is presented in the Appendix.

For a precise definition of DLPA consider a d-dimensional lattice. Particles hop randomly between nearest-neighbor lattice sites with constant rate D. When two particles meet on the same lattice site, they annihilate instantaneously. Generically, we assume some short range repulsive force, which has a consequence that particles hop onto occupied sites with a rate less than and independent of D. Equivalently one can assume a hard-core repulsion of particles and reaction with rate λ' when two particles meet on nearest-neighbor sites. Both processes are identical: in each case each lattice site can be occupied by at most one particle (in the first case because of the instantaneous annihilation of two particles, in the second case due to their hard-core repulsion) and pair annihilation takes *effectively* place on nearest-neighbor sites. The three-particle annihilation process is defined analogously.

We describe the stochastic dynamics in terms of a master equation for the time evolution of the probability $P(\eta,t)$ to find a particle configuration denoted by η at time t. A convenient representation of the master equation is in terms of a vector equation for the probability vector $|P(t)\rangle$, the so-called quantum Hamiltonian formalism (for a review see [20,23,24]). To each state of the system one assigns a basis vector $|\eta\rangle$ and its transpose $\langle \eta|$, which form an orthonormal basis of the vector space. The probability vector is then given by $|P(t)\rangle = \Sigma_\eta P(\eta,t)|\eta\rangle$ and the master equation can be cast in the form of an imaginary-time quantum mechanical Schrödinger equation,

$$\frac{d}{dt}|P(t)\rangle = -H|P(t)\rangle, \tag{1}$$

where the off-diagonal elements of the ''quantum Hamiltonian'' H are given by the transition rates $H_{\eta,\eta'} \equiv \langle \eta|H|\eta'\rangle = -w(\eta' \to \eta)$ and the diagonal elements are given by $H_{\eta,\eta} = \Sigma_{\eta' \neq \eta} w(\eta \to \eta')$. The off-diagonal terms of the Hamiltonian give the gain terms in the probabilty distribution $P(\eta,t)$ while the diagonal terms describe the loss of probability due to possible transitions out of the state η. The more conventional form of writing a general master equation can be recovered from Eq. (1) by multiplying from the left with $\langle \eta|$. The quantum Hamiltonian for the one-dimensional

version of this process is given in the Appendix where also the exact solution of the master equation for nonrepulsive particles is derived.

Modeling the (effective) absence of spatial correlations by the limit of infinite hopping rate leads to an enormous simplification of the master equation. The state of the system is then completely characterized by the probability of finding exactly N particles, rather than also by the spatial arrangement of these particles. The fast diffusion guarantees that the system randomizes very quickly and hence that always each N-particle spatial configuration is equally likely. The annihilation problem reduces now to that of calculating the probability of finding two particles simultaneously at a neighboring lattice site and annihilating them. Let $N(t)$ denote the total number of particles in the system at time t. The equation governing the evolution of $N(t)$ can be immediately written down as

$$\frac{d}{dt}\langle N(t)\rangle = -\lambda \sum_k \sum_{\langle\cdot\rangle} \langle n_k n_{k+\delta}\rangle, \qquad (2)$$

where the index k runs over all the lattice sites and the second sum runs over all the nearest-neighbor pairs of lattice sites. n_k is the number of particles at site k, which is either 0 or 1. The random number $n_{k+\delta}$ is the number of particles in the nearest-neighbor site of k. Since there are no correlations, we note that the probability of finding two particles on nearest-neighbor sites in a random configuration of N particles on M sites is equal to $N(N-1)/[M(M-1)]$.

In order to solve Eq. (2), we denote by $P(N,t)$ the probability of finding N particles in the system at time t, given that a total of M particles were distributed uniformly on the d-dimensional lattice at time $t=0$. Then the following consideration yields a master equation for time evolution of $P(N,t)$. The probability of finding exactly N particles increases by an annihilation event in a state with $N+2$ particles. The rate of change is proportional to the probability $(N+2)(N+1)/[M(M-1)]$ of finding two particles on nearest-neighbor sites in the $(N+2)$-particle state. On the other hand, the probability of finding exactly N particles decreases by an annihilation event in a state with N particles, with a rate proportional to $N(N-1)/[M(M-1)]$. Thus $P(N,t)$ obeys the following master equation:

$$\frac{d}{dt}P(N,t) = \mu \frac{(N+2)(N+1)}{M(M-1)} P(N+2,t)$$
$$- \mu \frac{N(N-1)}{M(M-1)} P(N,t), \qquad (3)$$

where μ is an effective time scale incorporating both the annihilation rate λ and the dimensionality of the system. This parameter is irrelevant for our study and in what follows we shall set $\mu=1$.

III. RANDOM WALK MODELING OF THE ANNIHILATION PROCESS

The annihilation dynamics described by the master equation (3) is readily mapped onto a directed random walk on a one-dimensional lattice as follows. We consider the number of particles in the system as the position of a random walker on a finite, one-dimensional lattice, indexed by integers from 0 to $M=2L$. Since two particles annihilate upon meeting, the random walk jumps two lattice sites to the left in one time unit. There is no right jump since there is only annihilation and no creation of particles. Equivalently we can consider a single-step random walk on the lattice $(0,L)$ with nearest-neighbor left jump rate

$$q_k = \frac{2k(2k-1)}{2L(2L-1)} \qquad (4)$$

at lattice site k, and the right jump rate is zero at all sites. It is clear that the left boundary (site 0) is absorbing. The random walk starts at site L. The position of the random walk at any time measures the number of particles at the time. Thus if the random walk is at lattice position k at time t, then it is equivalent to saying that there are $2k$ particles left in the system and $2L-2k$ particles have since been annihilated under the reaction. When the random walker reaches the absorbing site the pairwise annihilation has led to the extinction of the population. The fact that the left jump probability becomes less and less as one approaches the site 0 signifies that the annihilation events becomes rarer and rarer as the total number of particles decreases. It is this slowing down of the dynamics that leads to aging in the process, as we shall see shortly in the next two sections.

The random walk modeling of the three-particle annihilation process proceeds essentially in the same way. We assume $3L$ particles to be present at time $t=0$. In the random walk picture the annihilation corresponds to a jump of three sites to the left on a lattice of $3L$ sites until the system reaches the absorbing origin. Equivalently, the random walk executes nearest-neighbor jumps on the lattice $(0,L)$. The left jump probability at site k is

$$q'_k = \frac{3k(3k-1)(3k-2)}{3L(3L-1)(3L-2)}. \qquad (5)$$

As in the two-particle case there is no right jump, since particles are not created.

Note that in this mapping the form of the underlying lattice (in particular, its dimensionality) becomes irrelevant. Directed random walks have been investigated in a large variety of contexts [25], but there is no study on directed randoms walks with the transition probabilities (4), (5). In the following sections we consider these directed random walk models and show the presence of aging. For convenience we shall perform the calculation in discrete time by replacing in the master equation the time derivative by the finite difference $P(N,t+1)-P(N,t)$ and by considering the rates (which are probabilities per time unit) as actual hopping probabilities. As a technical point we remark that the normalization of the time scale chosen above ensures that no hopping probabilities larger than 1 or less than 0 are encountered in the time evolution of the system. The main feature of our treatment is the analysis in terms of the first passage time distribution.

IV. FIRST-PASSAGE-TIME FORMULATION AND AGING

Consider a lattice segment with the sites indexed by integers 0 to L. The random walk starts at site L. At any site $0 \leq k \leq L$, the left jump probability is q_k and the right jump probability is 0. The random walk eventually reaches the absorbing site 0. Following the technique described in [26] we define $\hat{G}_{k,k-1}(\nu)$ as the probability for a random walk to make a first passage from site k to site $k-1$ in exactly ν steps. Thus ν is the first passage time (FPT). A master equation for the FPT densities can be easily written as follows:

$$\hat{G}_{k,k-1}(\nu) = q_k \delta_{\nu,1} + (1-q_k)\hat{G}_{k,k-1}(\nu-1) \qquad (6)$$

for all $k = 1, L$. We introduce the generating function $G_{k,k-1}(z)$, for the FPT to go from k to $k-1$, and is defined as

$$G_{k,k-1}(z) = \sum_{\nu=1}^{\infty} z^{\nu} \hat{G}_{k,k-1}(\nu). \qquad (7)$$

Multiplying both sides of Eq. (6) by z^{ν} and summing over ν from 1 to ∞, we get

$$G_{k,k-1}(z) = \frac{z q_k}{1 - z(1-q_k)}. \qquad (8)$$

The right-hand side of the above equation can be expanded in powers of z, and the coefficient of z^{ν} yields the FPT density, $\hat{G}_{k,k-1}(\nu) = q_k(1-q_k)^{\nu-1}$. The required moments of FPT can be readily calculated from the FPT density. Equivalently, we can differentiate $G_{k,k-1}(z)$ with respect to z, for m times and set $z = 1$ to get the mth factorial moment of FPT from k to $k-1$. However, in this paper we are interested in motivating the presence of aging in the process, through the mean-first-passage times considerations. Accordingly, let $F_{k,k-1} = \langle \nu \rangle$ denote the MFPT. We get $F_{k,k-1} = G'_{k,k-1}(z=1) = 1/q_k$, where the prime denotes differentiation with respect to z. The MFPT to go from L to k is given by the sum

$$F_{L,k} = \sum_{m=k+1}^{L} \frac{1}{q_m}. \qquad (9)$$

We call $F_{L,k}$ the waiting time τ_w and $F_{k,k-1}$ the relaxation time τ_r and consider below how the relaxation time varies with the waiting time, for two- and three-particle annihilation processes.

For the two-particle annihilation process, as described in the last section, q_k is given by $2k(2k-1)/2L(2L-1)$. For large L, the relaxation time $\tau_r(k) \sim L^2/k^2$ and the corresponding waiting time $\tau_w(k) \sim L^2/k$. The largest waiting time is obtained for $k = 1$, for which $\tau_r = \tau_w \sim L^2$. As k runs from L to 1, i.e., as the walker approaches the absorbing state (or in other words, in the annihilation process, as the system approaches its state of extinction), both the relaxation and waiting times increase, a clear signature of aging in the process. Besides showing aging, the first-passage-time formulation gives an estimate of the range of waiting times over which one can expect aging to take place. Consider the FPT from L to 0, whose distribution is defined over the interval

(L, ∞); the minimum time required to reach the site 0 is L. Hence for waiting times greater than L one can expect aging to take place. The mean value of the FPT for going from L to 0 is of the order of L^2, for large L. Hence for waiting times in the range (L, L^2), the process would show aging scaling, as we shall demonstrate in the next section by calculating exactly the autocorrelation function.

For the three-particle annihilation process, we have $q_k = 3k(3k-1)(3k-2)/3L(3L-1)(3L-2)$. For large L, the relaxation time $\tau_r(k) \sim L^3/k^3$, and the corresponding waiting time $\tau_w \sim L^3/k^2$. Again, the largest waiting time is obtained when $k = 1$, for which $\tau_r = \tau_w \sim L^3$. As k runs from L to 1, we find that the relaxation time increases with the waiting time, indicating aging. Arguing along the same lines described in the last paragraph, we find that for the three-particle annihilation process, we can expect aging to take place over waiting times in the window (L, L^3). In the next section, we shall consider waiting times in this window, and show that the autocorrelation exhibits aging scaling. Generalizing, we argue that for m-particle annihilation process, we can expect aging over time scale from L to L^m.

The next task is to calculate numerically exactly the autocorrelation of the random walk process and to show that it depends only on the ratio of the two times for the time scales mentioned above. To this we turn now our attention.

V. CALCULATION OF THE AUTOCORRELATION FUNCTION

Let $P_k(t)$ denote the probability for the random walk to be at site k at time t given that it started off at L at time $t = 0$. The discrete time master equation for the evolution $P_k(t)$ is given by

$$P_k(t+1) = q_{k+1}P_{k+1}(t) + (1-q_k)P_k(t) \forall k = 0, L-1, \qquad (10)$$

$$P_L(t+1) = (1-q_L)P_L(t). \qquad (11)$$

This discrete master equation can be conveniently cast in a matrix notation by introducing a transfer matrix A:

$$|P(t+1)\rangle = A|P(t)\rangle, \qquad (12)$$

where the $(L+1)$-dimensional column vector $|P(t)\rangle$ has its kth element as $P_k(t)$ with k running from $0, L$, and A is the transition matrix. Let $\mu(t)$ and $\sigma(t)$ denote the mean and the standard deviation of the position of the random walk. These are calculated as follows:

$$\mu(t) = \langle S|\hat{X}A^t|P(0)\rangle, \qquad (13)$$

$$\sigma^2(t) = \langle S|\hat{X}^2 A^t|P(0)\rangle - \mu^2(t), \qquad (14)$$

where $\hat{X}$ is the state index operator given by diagonal matrix with elements $\hat{X}_{i,i} = i$; $\forall i = 0, L$. The *summing* vector $|S\rangle$ is $(L+1)$-dimensional with all its elements unity. $|P(0)\rangle = (00\cdots1)^T$ specifies the initial condition: $P_k(t=0) = \delta_{k,L} \forall k = 0, L$. The superscript T denotes transpose operation. The autocorrelation function of the position of the random walk (i.e., the temporal particle number autocorrelation function of the reaction-diffusion system)
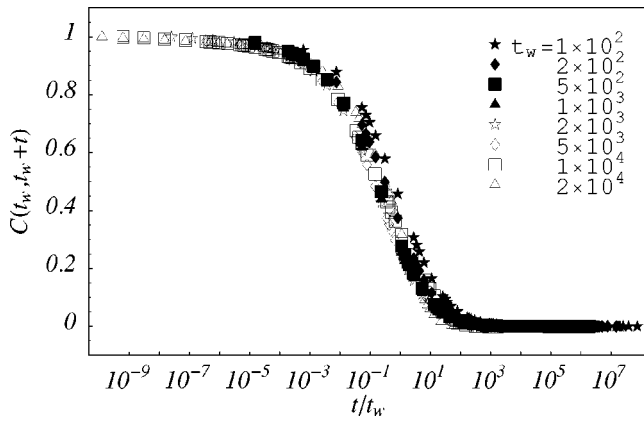
FIG. 1. Autocorrelation for various waiting times for the pair annihilation process.

$$C(t_w, t_w + t) = \frac{\langle S | \hat{X} A^t \hat{X} A^{t_w} | P(0) \rangle - \mu(t_w) \times \mu(t_w + t)}{\sigma^2(t_w)}, \quad (15)$$

can be evaluated on a computer employing straightforward matrix multiplication routines. We take the system size $L = 100$.

First we consider pair annihilation process. Figure 1 depicts the autocorrelation of the position of the random walk as a function of the ratio of t to t_w, for eight values of t_w ranging from L to $\approx L^2$, i.e., from 100 to 20 000. All the eight data sets collapse into a single curve, $C(t_w, t_w + t) = g(t/t_w)$, where the scaling function is unity for small values of the argument and which goes to zero for large values of the argument.

Figure 2 depicts the autocorrelation in the scaling variable for the problem of three-particle annihilation process. We have considered waiting times over the range, from L to L^3, i.e., from 100 to 1×10^6 time steps. Except for the data sets corresponding to $t_w = 100$ and $t_w = 1 \times 10^6$, the other six data sets collapse on a single scaling curve, showing that well within the window of waiting times between $t_w = L = 100$ and $t_w = L^3 = 1 \times 10^6$, the three-particle annihilation process exhibits the aging phenomenon.
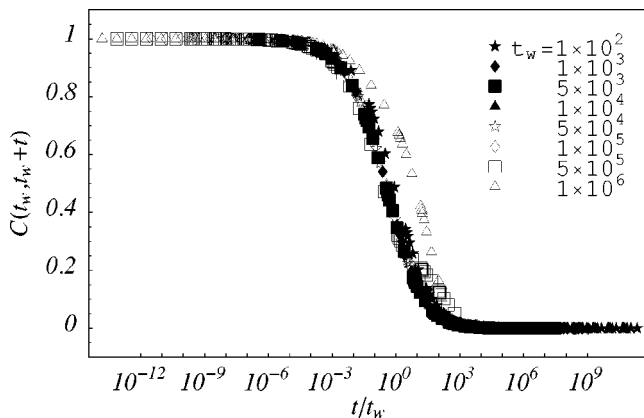

FIG. 2. Autocorrelation for the various waiting times for the three-particle annihilation process.

VI. CONCLUSIONS

In this paper we have examined the occurrence of aging in diffusion-limited annihilation processes. Arguing that correlations built up by insufficient diffusive mixing would help to confirm presence the aging, we have considered as a worst case scenario the limit of large diffusion rate as compared to the annihilation rate. In this limit, it is only the total number of surviving particles and not the spatial correlations, that determine the dynamics of the process. This limit is known to give a good approximation of annihilation reactions in three dimensions and we can map exactly the process onto a directed random walk on a one-dimensional lattice with an absorbing left boundary. From mean first passage time considerations we show that the relaxation time increases rapidly with aging times, signaling the presence of aging in the annihilation process. We have also calculated the autocorrelation function and shown that it scales with the ratio of the two times. In the appendix we show that, as expected, also annihilation processes with weak diffusive mixing show aging.

APPENDIX: DLPA IN ONE DIMENSION

Having found aging in annihilation processes with strong diffusive mixing it will come as no surprise to find it also in situations where the spatial correlations are relevant for the dynamics of the annihilation process. In DLPA in one dimension one finds anomalous slowing down of the kinetics, already predicted by Smoluchovsky [14] and much later confirmed by rigorous results [21]. The density decays as $t^{-1/2}$ rather than $\propto t^{-1}$ as is the case in three dimensions, a behavior clearly seen also in experiments involving exciton dynamics on long polymers [33]. We note that one knows from renormalization group investigations that a finite reaction rate and short range interaction forces are irrelevant for the behavior of the process [16]. Hence, without loss of information, one can assume particles to be physically noninteracting and annihilate with infinite reaction rate. The long-time behavior of this system is, to leading order in time, identical to that of a more realistic process with finite annihilation rate and some sort of short range interaction. For the one-dimensional case this equivalence is of interest as in this limit the problem is an exactly solvable many-body system.

Furthermore, in one dimension DLPA is equivalent to zero-temperature Glauber Ising dynamics [27] through a mapping from domain walls to particles [28,29]. This spin relaxation dynamics for the classical one-dimensional Ising ferromagnet describes growth of ferromagnetic domains after a quench from a high-temperature disordered initial state to zero temperature. Also from this point of view one expects aging to occur in this process. All that really remains to show is the explicit proof of aging in the context of the density

autocorrelation function and the calculation of the scaling form of $C(t_w+t, t_w)$.

For the calculation of the correlation function $\langle N(t_w + t)N(t)\rangle$ with a random initial state we follow the strategy developed in earlier work [30]. Here we just outline the main steps of the calculation. The quantum Hamiltonian for the master equation (1) reads

$$H = \frac{1}{2}\sum_k \left[(1-n_k)n_{k+1} - s_k^- s_{k+1}^+ + n_k(1-n_{k+1}) - s_k^+ s_{k+1}^- \right.$$
$$\left. + \lambda(n_k n_{k+1} - s_k^+ s_{k+1}^+)\right] \tag{A1}$$

with the Pauli matrices $s_k^\pm = (\sigma_k^x \pm i\sigma_k^y)/2$ and $n_k = (1 - \sigma_k^z)/2$. In this convention spin down at site k is identified with a particle, while spin up represents a vacancy. The reaction rate is given by λ and the hopping rate, which sets the time scale of the problem, has been chosen as $1/2$. Then $\lambda = 1$ corresponds to noninteracting particles, in which case the Hamiltonian can be expressed by means of a Jordan-Wigner transformation [31] in terms of free fermion operators [32].

After an additional Fourier transformation the Hamiltonian reads

$$H = \sum_p \left[(1-\cos p)b_p^\dagger b_p + \sin p\, b_{-p}b_p\right], \tag{A2}$$

where the $b_p^\dagger, b_p$ satisfy fermionic anticommutation relations. b_p annihilates the ''vacuum state'' $|0\rangle$ representing the empty lattice. For an even number of particles on a lattice of M sites p takes values $2\pi(k+1/2)/M$.

The quantity of interest is given by the expression

$$\langle N(t_w+t)N(t)\rangle = \langle s|Ne^{-Ht}Ne^{-Ht_w}|\rho_0\rangle \tag{A3}$$

with $N = \sum_k n_k$ and $|\rho_0\rangle$ denoting the uncorrelated initial state with density ρ_0. Without loss of generality we set $\rho_0 = 1$ corresponding to an initially full lattice. In terms of fermionic operators one finds $N = \sum_p b_p^\dagger b_p$ and $|\rho_0\rangle = \Pi_{p>0}b_{-p}^\dagger b_p^\dagger|0\rangle$. In [30] we showed that the subspace to which random initial conditions belong form an invariant subspace of H spanned by the bilinear zero-momentum excitations $B_p^\dagger = b_{-p}^\dagger b_p^\dagger$. Moreover, $B_p^\dagger$, B_p and $C_p = b_{-p}^\dagger b_{-p} - b_p^\dagger b_p$ commute for different p and satisfy the relations of spin-1/2 Pauli matrices $s^\pm, \sigma^z$ for equal values of p. Hence the time evolution within the random-initial state subspace factorizes into blocks of dimension 2 generated by the pair excitations $B_p^\dagger|0\rangle$. Thus the calculation of the correlator reduces to exponentiating the 2-by-2 matrices $H_p = (1-\cos p)N_p - \sin p\, B_p$ with $N_p = (1-C_p)/2$ [cf. Eq. (A2)] and then calculating

$$\langle N(t_w+t)N(t)\rangle = \sum_{p,p'>0}\prod_{q>0}\frac{\langle s|_q N_p e^{-H_q t}N_{p'}e^{-H_q t_w}|\rho_0\rangle_q}{\langle s|\rho_0\rangle_q},$$
$$\tag{A4}$$

where $\langle s|_p = \langle 0|(1+\cot(p/2)B_p)$ and for $\rho_0 = 1$ one has $|\rho_0\rangle_p = B_p^\dagger|0\rangle$. Choosing the basis such that $|0\rangle_p = (1,0)_p^T$ one finds $|1\rangle_p = (0,1)_p^T$, $\langle s|_p = (1,\cot(p/2))$ and

$$N_p = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \quad e^{-H_p t} = \begin{pmatrix} 1 & \cot(p/2)(1-e^{-2\epsilon_p t}) \\ 0 & e^{-2\epsilon_p t} \end{pmatrix}$$
$$\tag{A5}$$

with $\epsilon_p = 1 - \cos p$.

In the same way one calculates

$$\langle N(t)\rangle = \sum_{p>0}\prod_{q>0}\frac{\langle s|_q N_p e^{-H_q t}|\rho_0\rangle_q}{\langle s|\rho_0\rangle_q}. \tag{A6}$$

Denoting

$$\Lambda_p(t_w, t) \equiv \frac{\langle s|_p N_p e^{-H_p t}N_p e^{H_p(t_w+t)}|\rho_0\rangle_p}{\langle s|\rho_0\rangle_p} = e^{-2\epsilon_p(t_w+t)}$$

$$\Xi_p(t) \equiv \frac{\langle s|_p N_p e^{-H_p t}|\rho_0\rangle_p}{\langle s|\rho_0\rangle_p} = e^{-2\epsilon_p t} \tag{A7}$$

We are now in a position to calculate the two-time density correlation function

$$G(t, t_w) \equiv \langle N(t_w+t)N(t)\rangle - \langle N(t_w+t)\rangle\langle N(t_w)\rangle. \tag{A8}$$

Putting all intermediate results together one gets in the thermodynamic limit $L \to \infty$:

$$G(t, t_w) = \frac{1}{2\pi}\int_0^\pi dp[\Lambda_p(t_w, t) - \Xi_p(t_w+t)\Xi_p(t_w)]$$

$$= \frac{1}{2}(e^{-(2t_w+2t)}I_0(2t_w+2t)$$

$$- e^{-(4t_w+2t)}I_0(4t_w+2t)). \tag{A9}$$

Here $I_n(x)$ is the modified Bessel function of order n. For large argument $e^{-x}I_0(x) \sim 1/\sqrt{2\pi x}$. Normalizing the correlator as above by its value at $t=0$ and using the asymptotic expansion of the Bessel function finally gives the exact scaling function

$$C(t_w, t) = \frac{\sqrt{2/(1+x)} - \sqrt{2/(2+x)}}{\sqrt{2}-1} \tag{A10}$$

with the scaling argument $x = t/t_w$.

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