Nonequilibrium correlation functions in the $A + A \to \emptyset$ system with driven diffusion

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We solve the one-dimensional stochastic reaction-diffusion system $A + A \to \emptyset$ with *driven* diffusional relaxation and hard-core particles. Fluctuations in the total density (i.e., the mth moments $\langle N^m \rangle$ of the density distribution at any time $t \geq 0$) do not depend on the driving field, irrespective of the initial condition. For random initial conditions even local density fluctuations do not depend on the driving. A local perturbation in a random initial state evolves diffusively with a superimposed algebraic decay in time. The effect of the driving can be absorbed in a Galilei transformation.

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Stochastic reaction-diffusion processes in one dimension have become a major field of research in recent years. Being usually rather simple, they nevertheless show a very rich dynamical behavior and they are of both theoretical [1] and experimental [2,3] relevance in the study of far-from-equilibrium growth processes and reaction-diffusion systems. Among the best studied systems of this kind are the symmetric and asymmetric exclusion process [4], allowing only for (biased) diffusion, random sequential adsorption (RSA) [5], which is equivalent to annihilation of pairs of particles (without any diffusion), and Glauber dynamics [6], which at zero temperature maps to pair annihilation with diffusional relaxation [7]. What these three models have in common is that they all describe a system of interacting particles on a one-dimensional lattice, where each lattice site may be occupied by at most one particle. The interaction has two components. First, it is the exclusion principle which forbids double occupancy (a hard-core on-site repulsion) and secondly there is a nearest neighbor interaction describing the rate of change of any of the four possible configurations: Two vacant sites remain vacant, a single particle may hop to the vacant site to its right or left with rate $r_D = D(1 \pm \eta)/2$, and a pair of particles may react and annihilate with rate λ:

Process	Rate
$A\emptyset \to \emptyset A$	$D(1+\eta)/2$
$\emptyset A \to A\emptyset$	$D(1-\eta)/2$
$AA \to \emptyset\emptyset$	λ

Physically, the asymmetry in the left and right hopping rates may be thought of as the result of a field driving the particles in one preferred direction. If $\lambda = 0$ this is the asymmetric exclusion process, $D = 0$ corresponds to RSA, and $\eta = 0$, $\lambda = D$ maps to zero temperature Glauber dynamics [7].

The physics of these processes, however, is very different. The symmetric exclusion process ($\eta = \lambda = 0$) is, at least on the level of low order local correlation functions, not much different from its completely noninteracting counterpart. The dynamical exponent of the system is $z = 2$ and correlations decay algebraically to their stationary values. In the asymmetric case $\eta \neq 0$, however, the nonlinearity arising from the interaction becomes relevant. Local inhomogeneities lead here to the evolution of shocks [8]. The dynamical exponent for density correlations in a system with finite density is $z = 3/2$ [9]. In addition to that the phase diagram for both the steady state and dynamical behavior depends crucially on the boundary conditions imposed. Indeed, merely by changing boundary terms one may induce phase transitions between algebraic and exponential decay of correlations in space and time [10,11]. Other aspects which make this model interesting are its close relationship to growth processes, to polymers in random media, and to Burgers' equation [12].

An essential feature of RSA ($D = 0$) is the existence of jammed states, i.e., arbitrary configurations with no pairs of particles. Such a state cannot evolve further in time. Spatial correlations decay superexponentially [5].

Diffusion limited annihilation interpolates between these two models. The steady state is the completely empty lattice (if the system was at time $t = 0$ occupied by an even number of particles). With $\lambda = D$, i.e., the zero temperature Glauber case with biased domain wall diffusion, the system may be described in terms of free fermions and explicit and exact results for correlation functions become available: For the unbiased case the dynamical exponent for density correlations is known to be $z = 2$ and time-dependent correlations decay algebraically to zero [7,13–15]. This model is also of interest experimentally through a mapping to the coagulation process $AA \to A\emptyset$, $\emptyset A$ [16,17] which describes exciton dynamics on $N(CH_3)_4MnCl_3$ polymers [3]. Remarkably, the experimental exciton reaction and diffusion rates correspond to the free fermion condition $\lambda = D$ [17]. The density of excitons along the polymer $\rho(t) \sim t^{-y}$ decays algebraically. The measured value $y = 0.47(3)$ [3] agrees excellently with the known theoretical prediction from Glauber dynamics $y = 0.5$.

The biased case which we shall consider in this paper has been studied more recently [11,18–20]. The phenomenon of the boundary induced phase transition is known to persist for dynamical correlations [11]. For the free fermion case and with periodic boundary conditions exact results are available for the average density and the two-point correlation function for an initially fully occupied lattice [19]. These quantities turn out to be indepen-

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dent of η. For reaction rates $\lambda \neq D$ numerical simulations using random initial conditions do not show significant dependence of the behavior of the average density on the asymmetry, even for small values of the reaction rate λ [20].

These results for the average density are not surprising for the initial conditions considered. Because of translational invariance of both the initial state and the time evolution operator any local effects the driving may have are averaged over and therefore this quantity gives little insight into fluctuation effects in the presence of spatial inhomogeneities in the initial state. More challenging is the observation that also density correlations do not depend on the driving. Given the dramatically different behavior of the asymmetric exclusion process (without reaction) from the symmetric exclusion process, this is unexpected even for an initially full lattice and needs understanding. Unfortunately, there is no study on the impact of the driving either for uncorrelated random initial conditions with density $\rho_0 \neq 1$ or, what is even more interesting, for a nonhomogeneous initial distribution. It is clearly interesting to see to what extent the nonlinear effects known from the asymmetric exclusion process survive in the presence of the reaction and so to understand the interplay between hard-core repulsion, driving, and the nearest neighbor interaction. It is the aim of this paper to address these open problems for $\lambda = D$. The reason for this choice is twofold. First, the description in terms of free fermions allows for the explicit calculation of correlation functions. Secondly, the relationship to the coagulation problem as discussed in [16,17] allows for a translation of the results obtained here into results for coagulation and therefore for further predictions for exciton dynamics in experiments.

We define the process in terms of a master equation for the probability $f(\mathbf{n};t)$ of finding, at time t, any configuration $\mathbf{n}$ of particles in the system. Here $\mathbf{n} = \{n_1, n_2, \cdots, n_L\}$ where $n_i = 0, 1$ and $1 \leq i \leq L$ labels the sites of the lattice, and we assume periodic boundary conditions. We shall express the time evolution given by the master equation in terms of a quantum Hamiltonian H [21]. The advantage of this approach is that there are standard methods of dealing with the resulting time evolution operator H which do not arise naturally and obviously if the master equation is written down in standard form.

The idea is to represent each of the 2^L possible configurations in $X = \{0,1\}^L$ by a vector $|\,\mathbf{n}\,\rangle$. The probability distribution is then mapped to a state vector $|\,f(t)\,\rangle = \sum_{\mathbf{n}\in X} f(\mathbf{n};t)|\,\mathbf{n}\,\rangle$. The vectors $|\,\mathbf{n}\,\rangle$ together with the transposed vectors $\langle\,\mathbf{n}\,|$ form an orthonormal basis of $(C^2)^{\otimes L}$ and the time evolution is defined in terms of a "Hamilton" operator H by $\frac{\partial}{\partial t}|\,f(t)\,\rangle = -H|\,f(t)\,\rangle$ where $H = D\sum_{k=1}^{L} u_k$ with the nearest neighbor reaction matrices

$$\begin{aligned} u_k = {} & \frac{1+\eta}{2}\left[n_k(1-n_{k+1}) - s_k^+ s_{k+1}^-\right] \\ & + \frac{1-\eta}{2}\left[(1-n_k)n_{k+1} - s_k^- s_{k+1}^+\right] \\ & + \left(n_k n_{k+1} - s_k^+ s_{k+1}^+\right) \quad . \end{aligned} \tag{1}$$

Here $s_k^{\pm} = (\sigma_k^x \pm i\sigma_k^y)/2$ annihilate and create particles, respectively, and $n_k = 1/2\,(1-\sigma_k^z)$ are projection operators on states with a particle on site k of the chain. Using $f(\mathbf{n};t) = \langle\,\mathbf{n}\,|\,f(t)\,\rangle$ the master equation takes the form $\partial_t f(\mathbf{n};t) = -\langle\,\mathbf{n}\,|H|\,f(t)\,\rangle$. A state at time $t = t_0 + \tau$ is therefore given in terms of an initial state at time t_0 by

$$|\,f(t_0+\tau)\,\rangle = e^{-H\tau}|\,f(t_0)\,\rangle \quad . \tag{2}$$

Note that $\langle\,s\,|\,f(t)\,\rangle = \sum_{\mathbf{n}\in X} f(\mathbf{n};t) = 1$ where $\langle\,s\,| = \sum_{\mathbf{n}\in X}\langle\,\mathbf{n}\,|$ which expresses conservation of probability and which implies $\langle\,s\,|H = 0$. Expectation values $\langle\,n_{k_1}\cdots n_{k_N}\,\rangle$ of the local occupation numbers $n_k = 0, 1$ are given by the matrix elements $\langle\,s\,|n_{k_1}\cdots n_{k_N}|\,f(t)\,\rangle$. The master equation is solved either if (2) is solved for *any* $|\,f(0)\,\rangle$ or, alternatively, if one solves $n_k(t) = \exp(Ht)n_k\exp(-Ht)$.

One problem of physical interest is posed by the time evolution of uncorrelated random initial conditions with average density ρ, i.e., averages over all initial states where each N-particle configuration is weighted by the factor $(1-\rho)^{L-N}\rho^N$. Such an initial state is represented by the tensor product $|\rho\rangle = |\rho)^{\otimes L}$ with the column vector $|\rho) = (1-\rho, \rho)^T$. Another interesting quantity is the time-dependent fluctuation in the total density for arbitrary initial states, i.e., the moments $\langle N^m(t)\rangle/L^m$ of the density distribution where $N = \sum_k n_k$ is the number operator.

Without actually solving anything we can already derive two important results by noting the following. The Hamiltonian may be written $H = H_s + \eta H_d$ where the driving part H_d is given by $H_d = -D/2\sum_{k=1}^{L}(s_k^- s_{k+1}^+ - s_k^+ s_{k+1}^-)$ and H_s is the Hamiltonian for the system without driving. It is easy to check that $[H_d, H_s] = [H_d, N] = 0$ which immediately implies $N^m(t) \equiv \exp(Ht)N^m\exp(-Ht) = \exp(H_s t)N^m\exp(-H_s t)$. In other words, the time evolution of the density fluctuations does not depend on the driving, irrespective of the initial condition. Secondly, since $(1-\rho)s_k^+ - \rho(1-n_k)|\rho\rangle = \rho s_k^- - (1-\rho)n_k|\rho\rangle = 0$ one has $H_d|\rho\rangle = 0$. This implies $|\rho(t)\rangle \equiv \exp(-Ht)|\rho\rangle = \exp(-H_s t)|\rho\rangle$. Thus local density fluctuations $\langle\,n_{k_1}(t)\cdots n_{k_N}(t)\,\rangle$ at time t do not depend on the driving if random initial conditions with arbitrary density ρ are taken. Studying these quantities for the driven case gives nothing new compared to the same quantities for the undriven system [22]. This generalizes the results of Ref. [19].

In order to see what effect the driving actually has we study the time evolution of the local density $\rho_k(t) \equiv \langle n_k(t)\rangle$ for arbitrary initial conditions [23]. We define the operator $Q_k = \prod_{i=1}^{k}\sigma_i^z$ and perform a Jordan-Wigner transformation $a_k^\dagger = s_k^- Q_{k-1}$, $a_k = Q_{k-1}s_k^+$ [24]. These operators satisfy the anticommutation relations $\{a_k, a_l\} = \{a_k^\dagger, a_l^\dagger\} = 0$ and $\{a_k^\dagger, a_l\} = \delta_{k,l}$. Note that because of the periodic boundary conditions for the Pauli matrices one has $a_{L+1}^\dagger = a_1^\dagger Q_L$ and $a_{L+1} = Q_L a_1$. Q_L may be written $Q_L = (-1)^N$ where $N = \sum n_k$ is the number operator. Since by the action of H the particle number changes only in units of 2, Q_L commutes with H and splits it into a sector with an even number of parti-

cles ($Q_L = +1$) and into a sector with an odd number of particles ($Q_L = -1$). For definiteness we study only the even sector and assume also L to be even.

It is useful to introduce the Fourier transforms

$$b_p = \frac{e^{-i\frac{\pi}{4}}}{\sqrt{L}} \sum_{k=1}^{L} e^{\frac{2\pi i k p}{L}} a_k, \tag{3}$$

$$b_p^\dagger = \frac{e^{i\frac{\pi}{4}}}{\sqrt{L}} \sum_{k=1}^{L} e^{-\frac{2\pi i k p}{L}} a_k^\dagger \tag{4}$$

satisfying $\{b_p, b_q\} = \{b_p^\dagger, b_q^\dagger\} = 0$ and $\{b_p^\dagger, b_q\} = \delta_{p,q}$. Thus the representation of the number operator in Fourier space is

$$n_k = \frac{1}{L} \sum_{p,p'} e^{2\pi i k(p-p')/L} b_p^\dagger b_{p'} \ . \tag{5}$$

Here the sum runs over all integers $p = 0, \ldots, L-1$ in the sector with an odd number of particles and over the half odd integers $p = 1/2, 3/2, \ldots, L - 1/2$ in the even sector. The Hamiltonian now reads

$$H_s = \sum_p \left\{ \left(1 - \cos\frac{2\pi p}{L}\right) b_p^\dagger b_p + \sin\frac{2\pi p}{L} b_{-p} b_p \right\}, \tag{6}$$

$$H_d = -i \sum_p \sin\frac{2\pi p}{L} b_p^\dagger b_p \ . \tag{7}$$

Using this form of H shows that $b_p^\dagger(t)$ and $b_p(t)$ satisfy a set of only two coupled differential equations,

$$\frac{d}{dt} b_p^\dagger(t) = [H, b_p^\dagger(t)] = \epsilon_p b_p^\dagger(t) + 2\sin\left(\frac{2\pi p}{L}\right) b_{-p}(t), \tag{8}$$

$$\frac{d}{dt} b_p(t) = [H, b_p(t)] = -\epsilon_p b_p(t), \tag{9}$$

solved by

$$b_p^\dagger(t) = e^{\epsilon_p t} \left[b_p^\dagger + \cot\left(\frac{\pi p}{L}\right) \left(1 - e^{-(\epsilon_p + \epsilon_{-p})t}\right) b_{-p} \right], \tag{10}$$

$$b_p(t) = e^{-\epsilon_p t} b_p, \tag{11}$$

with $b_p^\dagger(0) = b_p^\dagger$, $b_p(0) = b_p$, and

$$\epsilon_p = 1 - \cos\left(\frac{2\pi p}{L}\right) - i\eta \sin\left(\frac{2\pi p}{L}\right). \tag{12}$$

This together with (5) gives $n_k(t)$ and, with specified initial conditions, any time-dependent correlation function at time t in terms of correlators at time $t = 0$.

For a study of the density profile $\langle n_k(t)\rangle$ it is convenient to compute its Fourier transform

$$S(q,t) = \frac{1}{L} \sum_{k=1}^{L} e^{2\pi i k q/L} \langle n_k(t)\rangle = \frac{1}{L} \sum_p e^{-(\epsilon_{-p} + \epsilon_{p+q})t} \cot\left(\frac{\pi p}{L}\right) \langle b_{p+q} b_{-p}\rangle \tag{13}$$

where we have used $\langle s|[b_p^\dagger + \cot(\pi p/L) b_{-p}] = 0$ [25]. For the calculation of the zero time correlator $\langle b_{p+q} b_{-p}\rangle$ one may further use

$$\langle b_{p+q} b_{-p}\rangle = \frac{i}{L} \sum_{k<l} (\alpha_{k,l} - \alpha_{l,k}) \langle n_k Q_k Q_{l-1} n_l\rangle \tag{14}$$

with $\alpha_{k,l} = \exp\{2\pi i[(k-l)p + kq]/L\}$. This gives the general solution for the average density at time t for an arbitrary initial state.

As discussed above, for a random initial condition with initial density ρ_0 the local density [equal to the global density $\rho(t) = \langle N(t)\rangle/L$ because of translational invariance] does not depend on the driving η. This in turn implies that for long times it will not depend on ρ_0 either [7]. We study therefore the time evolution of a local perturbation in a random initial distribution, i.e., we consider the initial state $n_L|\rho_0\rangle/\rho_0$ which is a random initial configuration where one finds a particle with probability $\rho_0 \neq 0, 1$ everywhere in the lattice except on site L where one has a particle with probability 1. This means that we study the quantity $\langle s|n_k \exp(-Ht) n_L|\rho\rangle$ which may also be interpreted as a two-time density-density correlation function $\langle n_k(t) n_L|(0)\rangle_\rho$ with an uncorrelated homogeneous initial state of density ρ. For technical simplicity we consider $\rho_0 = 1/2$ and project out the contributions with an odd number of particles, i.e., strictly speaking we consider the initial state $(1 + Q_L) n_L|\rho_0 = 1/2\rangle$. The zero time correlation function (14) is then given by

$$\langle n_k Q_k Q_{l-1} n_l\rangle = \begin{cases} (\delta_{l,k+1} - \delta_{k,1}\delta_{l,L-1})/4 & (l \neq L) \\ (\delta_{k,L-1} + \delta_{k,1})/4 & (l = L). \end{cases} \tag{15}$$

This gives

$$S(q,t) = \frac{\delta_{q,0}}{2L} \sum_p \left(1 + \cos\frac{2\pi p}{L}\right) e^{-(1-\cos 2\pi p/L)t} + \frac{1}{2L^2} \sum_p \left(1 - \cos\frac{2\pi(2p+q)}{L}\right) e^{-(\epsilon_{-p} + \epsilon_{p+q})t}. \tag{16}$$

In the first part of the sum one recognizes the known average density [14] at time t and the second part $\Delta S(q,t)$ gives the time evolution of the perturbation. By taking the limit $t \to \infty, L \to \infty$ with t/L^2 fixed one may derive the finite-size scaling form of $S(q,t)$. In the infinite volume limit $L \to \infty$ (with t fixed) one finds for $\Delta\rho_k(t) = \rho_k(t) - \rho(t)$

$$\Delta\rho_k(t) = \frac{1}{2\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} e^{-2i(kq - \eta t \sin q)} \times e^{-2t} \left[I_0(2\cos qt) - I_2(2\cos qt)\right] dq \tag{17}$$

where $I_n(x)$ are the modified Bessel functions of the first kind. This results shows that the effect of the driving can be completely absorbed in a lattice Galilei transformation [26], there is no evolution of shock waves. The dynamical exponent of the system remains $z = 2$ as in the absence of driving. In the scaling limit $t \to \infty, k \to \infty$ with k^2/t fixed (17) becomes

$$\Delta\rho_k(t) = \frac{1}{4\pi t^2} e^{-(k - \eta t)^2/t}, \tag{18}$$

representing a diffusive nature of the time evolution with a superimposed algebraic decay of the amplitude.

To conclude, we have studied the effect of driving in a simple reaction-diffusion system where exclusion particles hop with rates $(1 \pm \eta)/2$ to the right and left, respectively, if the nearest neighbor sites are empty and which are annihilated in pairs with rate 1 if the nearest neighbor site is occupied. We obtained the following results. (1) Fluctuations in the total particle number as a function of time do not depend on the driving parameter η, regardless of the initial condition. (2) Local time-dependent density fluctuations $\langle n_{k_1} \cdots n_{k_N} \rangle$ do not depend on η if uncorrelated random initial conditions have been taken. (3) In the scaling regime the effect of the driving on a local perturbation in a random initial state can be completely absorbed in a Galilei transformation; there is no evolution of shocks. (4) The time evolution of such a perturbation is diffusive, but with a faster decay of the amplitude ($\propto t^{-2}$ rather than $\propto t^{-1/2}$). These results have been obtained for annihilation rate $\lambda = 1$. It would be very interesting to study the system for other values of λ in order to understand the transition to the limiting cases $\lambda = 0$ (where the behavior of the system is dominated by the evolution of shocks) and $\lambda = \infty$ (where jammed states play an essential role). It may be worthwhile pointing out that our results indicate that it is not the exclusion principle as such which is responsible for the behavior of the system, but the strength of the pair interaction between neighboring particles. The generalization of these results to other initial conditions and average values are discussed elsewhere [25].

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