Dynamic Correlation Functions of Adsorption Stochastic Systems with Diffusional Relaxation

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We investigate the nonequilibrium behavior of dynamic correlation functions of random sequential adsorption processes with diffusional relaxation. Depending on the relative values of the transition probability rates, in one dimension these systems reduce to a soluble problem of many fermions. In contrast to the standard diffusive relaxation of the macroscopic density, the correlation functions exhibit a faster decay. Our results are supported and compared with Monte Carlo simulations.

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Lattice gas models involving random sequential adsorption (RSA) have attracted considerable interest due to their importance in many physical, chemical, and biological processes [1]. They can provide valuable insight into a broad class of far-from-equilibrium kinetic growth systems which have been studied intensively over the last decade [2]. The case of dimer deposition is typical and already exhibits very rich behavior. Recently, the interplay between random dimer filling and hopping of hard core particles has received systematic attention [3]. Here hopping allows isolated vacancies formed during dimer adsorption to diffuse together, creating empty pairs which have a finite lifetime and which may be filled at later stages of the stochastic evolution. Thus, the system is able to reach the completely filled adsorbing state. In one dimension, the density is known to relax diffusively as $t^{-1/2}$ for large times.

However, knowledge of the macroscopic concentration alone is not sufficient to describe the relative spatial distribution of particles and therefore to take into account fluctuation effects. The appropriate understanding of density fluctuations and nonequilibrium short-range and intermediate orders requires the use of more complicated averages characterizing the spatial particle correlations. Exact analyses of dynamic correlation functions have been given for a broad class of RSA processes [1], chemical reaction models [4], dynamics of diffusing hard core particles [5], and randomly hopping lattice gases [6]. As a contribution in this direction, here we present an exact solution of dynamic nonequilibrium, equal-time correlation functions of RSA systems with diffusional relaxation. It will turn out that such correlations relax faster than the density, i.e., as t^{-1} rather than diffusively.

The outline of our procedure is as follows. Using a (pseudo)spin description where spin up or down at a given site corresponds to particle or vacancy at that location, the stochastic evolution operator associated to the master equation [7] is then equivalent to the action of a quantum spin "Hamiltonian." For *certain* choices of transition rates, conservation of probability leads to the elimination of many-body terms from the Hamiltonian, which now is not Hermitian. A Jordan-Wigner transformation [8] makes it bilinear in fermion operators. Hence, a generalized Bogoliubov similarity transformation [9] allows its diagonalization, reducing it to a free fermion form. This enables us to determine nonequilibrium correlation functions by expanding the initial condition in terms of the eigenstates of the evolution operator. The complexities posed by the Jordan-Wigner transformation in higher dimensions [10] restrict our analysis to the one-dimensional case. Nevertheless, the case $d = 1$ already exhibits very rich behavior and shares the slow asymptotic kinetics observed in more general situations.

We now turn to the microscopic dynamical rules of our RSA model with diffusional relaxation. Pairs of nearest-neighbor sites of a linear chain are selected at random from N locations. A dimer adsorption attempt with rate ϵ takes place if the chosen sites are both vacant. Alternatively, hard core particles can hop on the chain, in principle with biased rates. Specifically, a particle at site j ($j + 1$) hops with rate h (h') provided the site $j + 1$ (j) is vacant. For future convenience and for reasons which will become clear, it is useful to introduce here an additional microscopic process, namely, attempts of dimer desorption with rate ϵ' which are successful whether or not the selected pair of adjacent particles arrived together. It will turn out that this fictitious construction has a well defined limit when ϵ' is set to zero at the very end of the calculation. Thus, our procedure can be formulated rigorously, and the final results will follow and correspond exactly to the original system. Further, they are in excellent agreement with Monte Carlo simulations.

Starting from the master equation [7] and using the constraint

$$\epsilon + \epsilon' = h + h', \tag{1}$$

the stochastic evolution of this system at time t is

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governed by the action of the Hamiltonian e^{-Ht}, namely,

$$H = -\epsilon \sum_j \sigma_j^+ \sigma_{j+1}^+ - \epsilon' \sum_j \sigma_j^- \sigma_{j+1}^- - \sum_j (h\sigma_{j+1}^+ \sigma_j^- + h'\sigma_j^+ \sigma_{j+1}^-) + (\epsilon' - \epsilon) \sum_j \sigma_j^+ \sigma_j^- + N\epsilon, \quad (2)$$

where σ_j^+ (σ_j^-) is a spin-$\frac{1}{2}$ raising (lowering) operator at site j. Adsorption (desorption) of dimers at rate ϵ (ϵ') is described by the action of the first (second) term, whereas hopping of hard core particles with rates h and h' is represented by the effect of the third and fourth terms in Eq. (2). Additionally, conservation of probability requires the appearance of diagonal terms while the constraint (1) ensures the cancellation of many-body interactions of the form $\sigma_j^+ \sigma_j^- \sigma_{j+1}^+ \sigma_{j+1}^-$.

As is known [8], the spin-$\frac{1}{2}$ operators can be mapped onto a set of spinless fermions via a Jordan-Wigner transformation. After Fourier transforming to wave fermions η_q it is straightforward to show that for periodic boundary conditions H reduces to the quadratic form

$$H = \sum_q [\omega_q \eta_q^\dagger \eta_q + \sin q(\epsilon \eta_{-q}^\dagger \eta_q^\dagger + \epsilon' \eta_q \eta_{-q}) + \epsilon],$$
$$\omega_q = a - b\cos q + i(h' - h)\sin q, \quad (3)$$

where $q = \pm\pi/N, \pm 3\pi/N, \ldots, \pm(N-1)\pi/N$, $a = \epsilon' - \epsilon$, and $b = \epsilon + \epsilon'$ [11].

We now consider the following Bogoliubov type similarity transformation [9]:

$$\begin{pmatrix} \xi_q^+ \\ \xi_{-q} \end{pmatrix} = \begin{pmatrix} \alpha \cos\theta_q & \alpha^{-1} \sin\theta_q \\ -\alpha \sin\theta_q & \alpha^{-1} \cos\theta_q \end{pmatrix} \begin{pmatrix} \eta_q^\dagger \\ \eta_{-q} \end{pmatrix},$$
$$\tan 2\theta_q = \frac{2\sqrt{\epsilon\epsilon'}\sin q}{b\cos q - a}, \qquad \alpha = \left(\frac{\epsilon}{\epsilon'}\right)^{1/4}, \quad (4)$$

which is well defined for *nonvanishing* transition rates ϵ, ϵ'. In terms of these operators, H can be cast as a free fermion Hamiltonian

$$H = \sum_q \lambda_q \xi_q^+ \xi_q, \quad \lambda_q = b - a\cos q + i(h - h')\sin q. \quad (5)$$

Thus, the introduction of the fictitious dimer desorption, discussed so far, takes into account the intrinsic non-Hermitian character of the evolution operator, making possible its straightforward diagonalization. However, notice that $\xi_q^+ \neq \xi_q^\dagger$, where $\dagger$ denotes Hermitian conjugation. Although the transformation (4) is not unitary, it can be easily checked that the operators ξ_q, ξ_q^+ are indeed fermion operators defined on right and left vacuum states $|\psi\rangle, \langle\tilde{\psi}|$ such that $\xi_q|\psi\rangle = 0$ and $\langle\tilde{\psi}|\xi_q^+ = 0$. Hence, $|\psi\rangle$ and $\langle\tilde{\psi}|$ are now identified as the corresponding right and left steady states whereas the elementary excitations $\xi_q^+|\psi\rangle$ are related to eigenstates decaying with a lifetime $\tau_q = (b - a\cos q)^{-1}$. It is worth pointing out in passing that $\mathrm{Re}\lambda_q > 0$, since by construction H is a stochastic matrix. In the limit $N \to \infty$ its spectrum exhibits a gap $g = 4\min(\epsilon, \epsilon')$ resulting from the creation of two elementary excitations [11], $\xi_{q0}^+ \xi_{-q0}^+ |\psi\rangle$ with $q_0 = 0^+$ if $\epsilon < \epsilon'$ or $q_0 = \pi^-$ if $\epsilon > \epsilon'$. Thus, for $\epsilon, \epsilon' \neq 0$ the asymptotic kinetics turns out to be exponentially fast as it is dominated by the existence of this gap. However, the limit $\epsilon' \to 0^+$ (or, alternatively, $\epsilon \to 0^+$) is special in that it gives rise to low-lying gapless modes which are ultimately responsible for the slow asymptotic behavior characteristic of RSA systems with diffusional relaxation.

Turning to the dynamic nonequilibrium correlation functions we recall that it is possible to express time-dependent averages in a simple way. As is known [12], for a given initial state $|\varphi_0\rangle$, the particle-particle connected correlations are given by

$$C_{l,m}(t) = G_{l,m}(t) - \rho_l(t)\rho_m(t),$$
$$G_{l,m}(t) = \langle\tilde{\psi}|\hat{n}_l \hat{n}_m e^{-Ht}|\varphi_0\rangle, \quad (6)$$
$$\rho_j(t) = \langle\tilde{\psi}|\hat{n}_j e^{-Ht}|\varphi_0\rangle,$$

where $G_{l,m}(t)$ is the joint probability of observing simultaneously a pair of particles at locations l and m (two-point correlations), whereas $\rho_j(t)$ is the average density of site j. Here, $\hat{n}_j \equiv \sigma_j^+ \sigma_j^-$ denotes the occupation number operator which in the ξ representation can be rewritten as

$$\hat{n}_j = \frac{1}{N} \sum_{k,k'} e^{i(k'-k)j} (\cos\theta_k \xi_k^+ - \sin\theta_k \xi_{-k}) \times (\cos\theta_{k'} \xi_{k'} - \sin\theta_{k'} \xi_{-k'}^+). \quad (7)$$

The crux of the analysis lies in the recognition that the initial state $|\varphi_0\rangle$ can be expanded in terms of the elementary excitations of the evolution operator. For the sake of simplicity, we will consider the case where the initial configuration characterizes an empty substrate. This is a very common situation within the context of RSA, thus it is of interest to elucidate the resulting dynamics of equilibration. Similar considerations will follow for more general situations, although for nontranslationally invariant (TI) initial states the algebra becomes rather heavy.

After straightforward manipulations it can be readily verified that the empty lattice corresponds to the coherent pair state

$$|\varphi_0\rangle = \prod_{0<q<\pi} (1 + \tan\theta_q \xi_q^+ \xi_{-q}^+)|\psi\rangle. \quad (8)$$

Therefore, recalling Eqs. (7) and (8) to determine the evolution of the density and the two-point correlations we are left with the calculation of

$$\rho_j(t) = \langle\tilde{\psi}|\hat{n}_j \left(1 + \sum_{0<q<\pi} e^{-2\mathrm{Re}\lambda_q t} \tan\theta_q \xi_q^+ \xi_{-q}^+\right)|\psi\rangle, \quad (9)$$

$$G_{l,m}(t) = \langle\tilde{\psi}|\hat{n}_l \hat{n}_m \left(1 + \sum_{0<q<\pi} e^{-2\mathrm{Re}\lambda_q t} \tan\theta_q \xi_q^+ \xi_{-q}^+ + \frac{1}{2!} \times \sum_{0<q,q'<\pi} e^{-2(\mathrm{Re}\lambda_q + \mathrm{Re}\lambda_{q'})t} \tan\theta_q \tan\theta_{q'} \xi_q^+ \xi_{-q}^+ \xi_{q'}^+ \xi_{-q'}^+\right)|\psi\rangle. \quad (10)$$

A word of caution should be added at this point. Although the similarity transformation (4) breaks down for vanishing desorption rates, it can be shown that the density and the correlation functions determined by Eqs. (9) and (10) have a well-defined limit when $\epsilon' \to 0$. The calculation is straightforward but lengthy. It is carried out using the anticommutation rules associated with the Fermi operators ξ_q and ξ_q^+ which are well defined so long as $\epsilon, \epsilon' \neq 0$. Also, higher-order (many-particle) correlation functions can be treated by generalizations of this methodology. *After* taking the limit $\epsilon' \to 0$ the final result is

$$\rho_j(t) = \rho(t) = 1 - e^{-2\epsilon t} I_0(2\epsilon t), \tag{11}$$

$$C_n(t) = -e^{-4\epsilon t} I_n^2(2\epsilon t) - F_n^+(2\epsilon t)[(-1)^n + F_n^-(2\epsilon t)], \tag{12}$$

where $I_0(z), I_n(z)$ are modified Bessel functions of integer order $n = |l - m|$ and

$$F_n^{\pm}(z) = \frac{e^{-z}}{\pi} \int_0^{\pi} \frac{e^{-z\cos q}}{\sin q} \sin nq(1 \pm \cos q)\, dq\,. \tag{13}$$

We direct the reader's attention to Fig. 1 where we display our Monte Carlo simulations. Setting $\epsilon' \equiv 0$, the microscopic dynamical rules discussed above were repeated N times, after which the time was increased by one unit. Of course, intermediate measurements of time intervals not smaller than $1/N$ can also be attained. The averages were taken over 2×10^3 histories of an initially empty chain with $N = 10^5$ sites and periodic boundary conditions. This has been adequate to suppress fluctuations and finite size effects. The agreement with the theoretical result given by Eq. (12) is remarkable.

The bias in the hopping rates enters neither the forms of the density nor the correlation functions [so long as the constraint (1) is fulfilled], as opposed to the form of unequal-time functions (e.g., autocorrelations) where the bias enters in a rather complex way [13]. Since we have taken an initially empty lattice, the correlations (12) remain TI for all subsequent times. However, non-TI initial conditions with long-ranged correlations might eventually introduce significant changes, of logarithmic type at the very least [13].

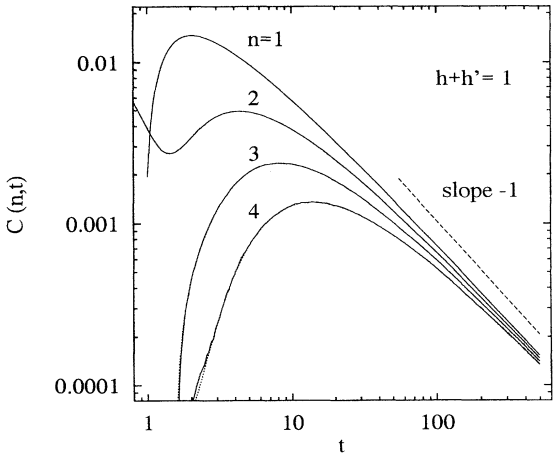

FIG. 1. Nondiffusive decay of equal-time connected correlation functions for $\epsilon = 1$ and $h = h' = 0.5$. The averages were taken over 2×10^3 histories starting from an empty lattice of 10^5 sites. The numerical data (solid lines) reproduce completely the theoretical results given by Eq. (12) in the text (dotted lines slightly observable at the bottom left).

Although the integrals (13) are difficult to evaluate in terms of known special functions, nonetheless we can extract their asymptotic behavior. In the scaling regime where $n \to \infty$, $t \to \infty$ with n^2/t held finite, we obtain

$$\rho(t) \simeq 1 - \frac{1}{2\sqrt{\pi \epsilon t}}\,, \qquad C_n(t) \simeq -\frac{e^{-n^2/2\epsilon t}}{4\pi\epsilon t} + \mathcal{O}(n/t^{3/2})\,. \tag{14}$$

Thus, the macroscopic density relaxation exhibits the standard diffusive long time tail $\sim t^{-1/2}$, whereas the asymptotic behavior of particle-particle correlations turns out to be anomalous in the sense that they decay faster than diffusively, namely, as t^{-1} (see Fig. 1). It is interesting to see how such correlations build up a diffusive correlation length ξ along with the emergence of a self-similar growth pattern. This is clearly seen from Eq. (14) as it is immediate to show that for large times and long wavelengths $\sim k^{-1}$ the nonequilibrium structure factor $S(k,t)$ satisfies time-dependent scaling

$$S(k,t) \simeq \mathcal{F}[k\xi(t)]/\xi(t)\,, \tag{15}$$

where the scaling function $\mathcal{F}$ and the correlation length ξ are given by

$$\mathcal{F}(z) = -\frac{e^{-z^2/2}}{\sqrt{8\pi}}\,, \qquad \xi(t) = (\epsilon t)^{1/2}. \tag{16}$$

Hence, macroscopic density fluctuations $\propto S(0,t)$ decay diffusively as $t^{-1/2}$. Notice that $\xi(t)$ is also a measure of the average linear domain size which grows as $t^{1/2}$.

Our results have important consequences for the kinetics of adsorption rates $R_a(t) = \langle\tilde{\psi}|(1 - \hat{n}_j)(1 - \hat{n}_{j+1})e^{-Ht}|\varphi_0\rangle$, one of the main experimentally measurable quantities. This is the fluctuation equivalent to the mean-field statement that the rate of adsorption is proportional to the number of vacancies in the nearby contact. Alternatively, this (reduced) rate can be obtained from $d\rho/dt$. From Eqs. (11) and (12) it follows that

$$R_a(t) = e^{-2\epsilon t}[I_0(2\epsilon t) - I_1(2\epsilon t)] \simeq \frac{(\epsilon t)^{-3/2}}{8\sqrt{\pi}} + \mathcal{O}(t^{-5/2}), \qquad \epsilon t \gg 1\,. \tag{17}$$

Therefore, the adsorption rate decreases asymptotically with the cube of the average domain size, i.e., $R_a \sim \xi^{-3}$.

It is appropriate to note that models involving RSA with diffusional relaxation are isomorphic to problems involving irreversible desorption in competition with surface migration. Specifically, for the case of dimers, when two isolated vacancies are brought together, either they can

be covered by an incoming dimer and disappear or they can separate again due to diffusion. Then the single-site vacancies, labeled $\mathcal{A}$ say, are effectively following the reaction-diffusion process $\mathcal{A} + \mathcal{A} \rightarrow$ inert. Such processes have been studied extensively in the literature [14], thus, it is worth pointing out that our conclusions apply to those systems as well. Specifically, Eq. (12) corresponds exactly to the pair correlation functions of these systems (with ϵ replaced by ϵ') starting from an initially full lattice. Also, the constraint (1) turns out to be the condition for our model to be equivalent to a generalized single spin flip Glauber dynamics [15] in a description in which kinks $s_j s_{j+1}$ ($s_j = \pm 1$) or domain walls correspond to particle occupation numbers $n_j = (1 - s_j s_{j+1})/2$ [16]. However, note that the particle-particle correlations functions $C_n(t)$ considered so far are highly nontrivial to determine in such dual language as for $n > 1$ they require the evaluation of four-spin correlations $\langle s_j s_{j+1} s_{j+n} s_{j+n+1} \rangle$ in the Glauber model. In contrast, our methodology is more efficient to accomplish this purpose and may be encompassed within the Felderhof approach to the one-dimensional kinetic Ising model [17].

If the constraint (1) is dropped, no way of solving this general situation is presently known. However, it is likely that the elementary excitations have a gap [13]. There are other special cases in which simple correlation functions can be found. The principal ones are $\epsilon = \epsilon' = 0$ (diffusion), or $h = h' = 0$ (adsorption or desorption). The case treated in this work is another and is actually more general in having only one constraint rather than two. It is exactly soluble for any correlation function and includes a crossover from gap to zero gap (as $\epsilon' \rightarrow 0$ or $\epsilon \rightarrow 0$). Also, while the gapless behavior of the other standard cases can be inferred from Goldstone arguments, that is not possible for the present model.

In summary, we have reformulated the calculation of nonequilibrium correlation functions in RSA systems with diffusional relaxation as a soluble problem of many fermions. Generalizations of our results to higher dimensions are clearly of theoretical and experimental interest. The anomalous relaxation of pair correlations could be an effect related ultimately to the one-dimensional nature of this process in which fluctuations are more profound. The issue as to whether or not these dynamic correlations exhibit such behavior for $d > 1$ remains quite open.

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