Dynamics of adsorption-desorption processes as a soluble problem of many fermions

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We study the nonequilibrium dynamics of one-dimensional adsorption-desorption processes with diffusional relaxation. According to the relative values of the transition probability rates, these systems can be mapped onto a soluble problem of many fermions. The time development of pair correlations, interparticle distribution functions, macroscopic density, structure factor, and density fluctuations is obtained by combining and comparing both exact results with Monte Carlo simulations. Depending on the spectrum gap of the evolution operator associated with the stochastic dynamics, these quantities display either exponential decay or power-law relaxation. For vanishing gaps, the pair correlations exhibit a faster decay as opposed to the standard diffusive relaxation of the macroscopic density.

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I. INTRODUCTION

There has been much current interest in stochastic systems in situations where traditional classical (mean field) rate equations do not apply [1]. A standard example of such a fluctuation-dominated case is the diffusion-reaction system under conditions, e.g., low dimensionality, where the diffusion of reactants is not sufficiently rapid, compared to the reaction rate, to suppress spatial concentration fluctuations [2]. Another source of fluctuation phenomena is the discreteness of local particle number, e.g., at a given site in lattice-based theories. Lattice descriptions are convenient for the incorporation of hard-core particle interaction effects, through "exclusion" models in which each site can be at most singly occupied [3]. Through a pseudospin representation of the site occupation these exclusion models can be mapped to quantum spin models [4,5].

Since fluctuation effects are most pronounced in dimensionality $d = 1$, much attention is currently focused on that case. One-dimensional models of course have a greater chance of exact solution, while still being far from trivial, i.e., quantum spin chains are often related to equilibrium two-dimensional classical models, and can have analogous phase transitions in their ground state and other cooperative effects [6]. The present paper is concerned with exact solutions for a generalized type of one-dimensional stochastic model which turns out to have rich fluctuation behavior. A recent work has shown that it is related by various mappings to a wide variety of other models [7].

The processes explicitly included are (i) adsorption or desorption (with independent rates ϵ and ϵ') of particles in pairs on adjacent sites; and (ii) single particle diffusion which for complete generality is allowed to be asymmetric (hopping rates h and h' to right and left, respectively), for example, as a result of some driving mechanism. The "dimer" adsorption and desorption processes alone have already been shown [5] to be interesting in having slow dynamics related to a Goldstone symmetry, and (for $\epsilon = \epsilon'$) an exact solution has previously been provided for the pair correlation via a pseudospin description in which a sublattice mapping takes the evolution operator to the Heisenberg model Hamiltonian [5]. The addition of the diffusion process gives an idealized model for catalysis.

The generalized model with processes (i) and (ii) includes as special cases the Flory dimer-deposition problem [8], biased diffusion [9], random sequential adsorption with diffusional relaxation [3], etc. Sublattice mappings or more general pseudospin rotations take the generalized model into a large set of other general models including coagulation and single-particle production and annihilation processes [7]. Despite its idealized nature, it therefore has the possibility of wide experimental relevance [10]. To extract the main characteristic phenomena, and for possible experimental comparisons, various types of particle correlation function in space and time are of interest, as well as the scattering and structure functions obtained by Fourier transformation [11]. So in this paper exact results are given for time-dependent pair correlations, interparticle distribution functions, density, density fluctuations, and structure factors.

Exact solutions of this type turn out to be possible only under special conditions. Special soluble cases previously treated are (a) the dimer adsorption-desorption problem referred to previously [5] ($\epsilon = \epsilon,' h = h' = 0$), and (b) symmetric diffusion of hard-core particles ($h = h'$, $\epsilon = \epsilon' = 0$) [12]. These two cases are related by sublattice mapping [5,13].

The soluble case treated here is the general process of adsorption and desorption with driven diffusion, but with one constraint relating rates, namely, $\epsilon+\epsilon' = h+h'$.

This is the condition under which the evolution operator of the system can be converted to a *free*-fermion form by a Jordan-Wigner transformation [14] on the quantum spin Hamiltonian of the pseudospin description. A generalized Bogoliubov-Valatin type transformation of fermion operators [15] then allows a complete solution.

To investigate the effects of relaxing the constraint $\epsilon + \epsilon' = h + h'$, Monte Carlo simulations of cases with $\delta \equiv \epsilon + \epsilon' - h - h' \neq 0$ are also provided here. They show no substantial change from the $\delta = 0$ soluble case, suggesting that this case is actually generic. It is also interesting that the free-fermion condition $\delta = 0$ is also the condition for the equivalence of the model to a generalized single-spin-flip Glauber dynamics [13,16]; and that the soluble case includes a subcase $\epsilon = \epsilon' = h = h'$ equivalent to the one-dimensional equilibrium Ising model and therefore soluble by standard transfer matrix techniques.

The system discussed here also includes a very important special case $\epsilon' = 0$ (or $\epsilon' = 0$) in which only desorption (or adsorption) occurs with driven diffusion. This is equivalent to the reaction-diffusion process $A + A \rightarrow$ inert, so our results apply to this interesting case [17]. Since the Bogoliubov transformation used in the diagonalization of the free-fermion Hamiltonian is singular for ϵ (ϵ') $= 0$ (see Sec. II) this case is obtained via a limit $\epsilon' \rightarrow 0$. A brief account has been given elsewhere [18] of some of the $\epsilon' \rightarrow 0$ results. The present paper provides details necessarily omitted from that account as well as additional results. Monte Carlo simulations provide a confirmation of the analytic results obtained, as well as some extensions, such as the investigation of the generalized case $\delta \neq 0$ which suggests the robustness of the soluble case.

The structure of this work is as follows. Section II presents the master equation and transition processes, the representation of these by a quantum spin Hamiltonian, and the mapping to a fermion system. The free-fermion reduction and Bogoliubov transformation are also given here, as well as comments on the asymptotic form of decays and the role of symmetries. Dynamical pair correlation functions are calculated in Sec. III. Explicit analytic results and asymptotic behaviors are given here, and compared to Monte Carlo simulations. The case $\epsilon' \rightarrow 0$ is also treated here. Section III also contains the Monte Carlo check on the robustness of the $\delta = 0$ results. Section IV gives an analytic calculation of the interparticle distribution function in a simple situation, and Monte Carlo simulations of the general case. Section V is a discussion of the work. An Appendix gives calculational details omitted from Sec. III.

II. STOCHASTIC DYNAMICS, QUANTUM SPIN CHAINS, AND FERMION MODELS

In this section we describe the basic stochastic steps. As stated in Sec. I, our analysis will be limited to the one-dimensional case. The microscopic dynamical rules defining the stochastic evolution of our adsorption-desorption (AD) model are as follows. Pairs of nearest-neighbor sites of a linear chain are selected at random from N locations. A dimer adsorption (desorption) attempt with rate ϵ (ϵ') takes place if the chosen sites are both vacant (occupied). Alternatively, hard-core particles can hop on the chain with biased rates. Specifically, a particle at site j ($j+1$) hops with rate h (h') provided the site $j+1$ (j) is vacant. By construction these processes are uncorrelated and mutually exclusive. Notice that the rule of desorption along with particle diffusion does not preserve the *identity* of dimers during the AD process. Dimers can evaporate with rate ϵ' whether or not the selected pair of adjacent particles arrived together. Therefore this dynamics leads to a continuous redistribution of particles giving rise in turn to reconstruction of dimers. In Fig. 1 we show a snapshot of a particular evolution resulting from these microscopic rules. Further details will be given in Sec. III A.

As is known [19], the probability distribution $P(s,t)$ to observe the system in a particular configuration $|\, s \,\rangle$ at time t is governed by a master equation. Starting from an initial state $|\, P(0) \,\rangle \equiv \sum_s P(s,0)\,|\, s \,\rangle$ such an equation can be written in the operational form $|\, P(t) \,\rangle = e^{-Ht}\,|\, P(0) \,\rangle$ [20]. Here, the evolution operator H is build up in terms of the transition probability rates $W(s \rightarrow s')$ contained in its matrix elements, namely,

$$\begin{aligned} \langle\, s' \,|\, H \,|\, s \,\rangle &= -W(s \rightarrow s')\,, \quad s' \neq s\,, \\ \langle\, s \,|\, H \,|\, s \,\rangle &= \sum_{s' \neq s} W(s \rightarrow s') \quad , \\ \{W(s \rightarrow s')\} &= \{\epsilon, \epsilon', h, h'\}\,. \end{aligned} \tag{1}$$

Hence, the left steady state $\langle\, \tilde{\psi} \,|$ can be constructed as an equally weighted linear combination of all reachable configurations as $\sum_{s'} \langle\, s' \,|\, H \,|\, s \,\rangle \equiv 0$. Conservation of probability therefore requires the normalization condition

$$\sum_s \langle\, s \,|\, e^{-Ht}\,|\, P(0) \,\rangle = \langle\, \tilde{\psi} \,|\, P(t) \,\rangle = 1 \quad \forall\, t \geq 0\,. \tag{2}$$

A. Spin chains

The analysis of the master equation becomes systematic after characterizing particles and vacancies respec-

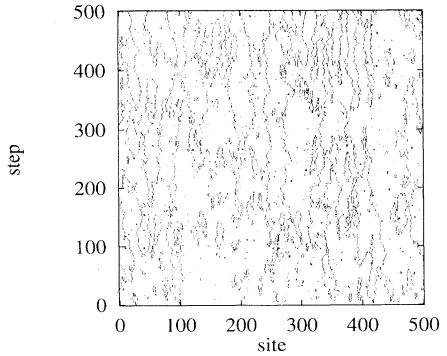

FIG. 1. Snapshot of the associated stochastic evolution for $\epsilon = 0.05, \epsilon' = 0.8$, and $h = h' = 0.5$. On average each lattice bond is exchanged once per unit time. Details of the simulation procedure are described in Sec. III A.

tively by the $\frac{1}{2}$ spinors $\alpha_z = \binom{1}{0}$ and $\beta_z = \binom{0}{1}$, for instance in the σ^z representation. In such language, the set of probability rates related to our AD microscopic rules (acting on sites $j, j+1$, say) corresponds to the following spin-flip processes:

$$\begin{aligned}
&\beta_z(j)\,\beta_z(j+1) \xrightarrow{\epsilon} \alpha_z(j)\,\alpha_z(j+1)\,,\\
&\alpha_z(j)\,\alpha_z(j+1) \xrightarrow{\epsilon'} \beta_z(j)\,\beta_z(j+1)\,,\\
&\alpha_z(j)\,\beta_z(j+1) \xrightarrow{h} \beta_z(j)\,\alpha_z(j+1)\,,\\
&\beta_z(j)\,\alpha_z(j+1) \xrightarrow{h'} \alpha_z(j)\,\beta_z(j+1)\,.
\end{aligned} \tag{3}$$

Hence the stochastic dynamics is associated with the "Hamiltonian" of a quantum spin-$\frac{1}{2}$ chain whose action keeps proper track of all transition rates involved in (3). This approach enables us to exploit alternative calculation schemes (see below) which are specifically useful to investigate nonequilibrium features, in particular nonequilibrium correlation functions. Using the σ^x, σ^y, σ^z spin-$\frac{1}{2}$ Pauli matrices, and after introducing the parameters

$$a = \epsilon' - \epsilon\,,\quad b = \epsilon' + \epsilon\,,\quad c = h' - h\,,\quad d = h' + h\,, \tag{4}$$

the evolution operator which reproduces the matrix elements (1) turns out to be

$$\begin{aligned}
H = &\frac{1}{4}(b-d)\sum_j \left(\sigma_j^z\,\sigma_{j+1}^z + \sigma_j^y\,\sigma_{j+1}^y\right)\\
&-\frac{1}{4}(b+d)\sum_j \left(\sigma_j^x\,\sigma_{j+1}^x - 1\right)\\
&+\frac{a}{2}\sum_j \sigma_j^z + \frac{i}{4}(a+c)\sum_j \sigma_j^x\,\sigma_{j+1}^y\\
&+\frac{i}{4}(a-c)\sum_j \sigma_j^y\,\sigma_{j+1}^x\,.
\end{aligned} \tag{5}$$

This form of Hamiltonian arises from having represented dimer adsorption, dimer desorption, and single-particle hopping by the action of the nondiagonal terms of H. It is a simple matter to check that these terms provide precisely the spin-flip transitions (3). Since these processes occur with rates $\epsilon, \epsilon', h, h' \leq 1$, conservation of probability requires in addition the appearance of diagonal (many body) terms. There are three special cases in which the nonequilibrium dynamics can be analyzed extensively. The principal ones are (i) $\epsilon = \epsilon' = 0$ (biased diffusion) [9], (ii) $h = h' = 0$ (pure AD) [5], and (iii) $\epsilon + \epsilon' = h + h'$ (AD with diffusional relaxation). The character of the asymptotic behavior of (i) and (ii) is already determined by the symmetries involved in (5). Specifically, we recall that under a rotation by an angle φ around the spin z axis, the transverse spin operators transform as tensors of rank 1. Thus for cases (i) and (ii) it can be readily verified that H remains invariant by the similarity transformation $S(\varphi)\,H\,S^{-1}(\varphi)$, where

$$S(\varphi) = \begin{cases} \exp\left[i\,\frac{\varphi}{2}\sum_j \sigma_j^z\right]\,, & \epsilon = \epsilon' = 0\\[2ex] \exp\left[i\,\frac{\varphi}{2}\sum_j (-1)^j\,\sigma_j^z\right]\,, & h = h' = 0\,. \end{cases} \tag{6}$$

Since the steady (ground) state of H *breaks* this continuous symmetry [5], the Goldstone theorem implies the existence of low-lying gapless modes which are ultimately responsible for the emergence of a slow asymptotic dynamics. In particular, for $\epsilon = \epsilon'$, $h = h' = 0$ or $h = h'$, $\epsilon = \epsilon' = 0$, it can be shown that after appropriate sublattice mappings the evolution operator reduces to the fully rotational invariant isotropic Heisenberg ferromagnet. In such cases, the dispersion relation of the single spin-wave excitations gives rise to diffusive behavior for large time regimes [5].

B. Fermion systems

While the gapless character of (i) and (ii) can be inferred by Goldstone arguments, it is difficult to apply such considerations to arbitrary probability rates. However, case (iii) is still amenable to an extensive analytic treatment. The key issue lies in the recognition that for $\epsilon + \epsilon' = h + h'$ there is a cancellation of many body interactions in Eq. (5). In terms of the spin-$\frac{1}{2}$ raising and lowering operators $\sigma^+ = (\sigma^x + i\sigma^y)/2$ and $\sigma^- = (\sigma^x - i\sigma^y)/2$, this constraint yields the following quadratic form:

$$\begin{aligned}
H = &-\epsilon\sum_j \sigma_j^+\,\sigma_{j+1}^+ - \epsilon'\sum_j \sigma_j^-\,\sigma_{j+1}^-\\
&-\sum_j \left(h\,\sigma_{j+1}^+\,\sigma_j^- + h'\,\sigma_j^+\,\sigma_{j+1}^-\right)\\
&+(\epsilon' - \epsilon)\sum_j \sigma_j^+\,\sigma_j^- + N\epsilon\,.
\end{aligned} \tag{7}$$

As is well known, this problem can be mapped onto a set of spinless fermion operators $C_n^\dagger$, C_n via a Jordan-Wigner transformation [14]. Due to parity conservation, the kinetics is restricted to take place within two subspaces having either an even or odd number of particles. For the sake of simplicity and because of its relevance within the context of AD cooperative processes, in what follows we shall analyze the stochastic dynamics resulting from an initially empty lattice (evolving through the even sector). In such a case, assuming periodic boundary conditions the Jordan-Wigner transformation imposes anticyclic requirements when applied to the even subspace, i.e., $C_{N+1} = -C_1$, $C_{N+1}^\dagger = -C_1^\dagger$. As usual, it is convenient to Fourier transform to running wave fermions η_q,

$$\eta_q = \frac{e^{-i\pi/4}}{\sqrt{N}}\sum_n e^{-iqn}\,C_n\,. \tag{8}$$

To satisfy the above anticyclic conditions the wave

numbers q should take the values of the set $Q = \{\pm\pi/N, \pm 3\pi/N, \ldots, \pm(N-1)\pi/N\}$ where we have assumed for convenience that N is even. In terms of the wave operators η_q, it can easily be found that

$$H = \sum_{q\in Q}\Big[\omega_q\,\eta_q^\dagger\,\eta_q + (\sin q) \times\Big(\epsilon\,\eta_{-q}^\dagger\,\eta_q^\dagger + \epsilon'\,\eta_q\,\eta_{-q}\Big) + \epsilon\Big],$$
$$\omega_q = a - b\cos q + ic\sin q, \tag{9}$$

where the parameters a, b, and c are taken as in Eq. (4)

For *nonvanishing* transition rates ϵ and ϵ' the diagonalization and the non-Hermitian character of the evolution operator (9) can both be taken into account by the following Bogoliubov type similarity transformation [15]:

$$\xi_q^+ = \alpha(\cos\theta_q)\,\eta_q^\dagger + \alpha^{-1}(\sin\theta_q)\,\eta_{-q},$$
$$\xi_{-q} = \alpha^{-1}(\cos\theta_q)\,\eta_{-q} - \alpha(\sin\theta_q)\,\eta_q^\dagger, \tag{10}$$

where α and the (real) angles θ_q are given by

$$\alpha = \left(\frac{\epsilon}{\epsilon'}\right)^{1/4}, \quad \tan 2\theta_q = \frac{2\sqrt{\epsilon\,\epsilon'}\,\sin q}{b\cos q - a}. \tag{11}$$

For $\epsilon \neq \epsilon'$ this transformation is not unitary. Even so, it can be readily verified that the ξ operators satisfy fermionic anticommutation rules. However, notice that $\xi_q^+ \neq \xi_q^\dagger$ where $\dagger$ denotes Hermitian conjugation. In terms of these operators H can be finally cast as the free-fermion Hamiltonian

$$H = \sum_{q\in Q}\lambda_q\,\xi_q^+\,\xi_q, \quad \lambda_q = b - a\cos q + ic\sin q. \tag{12}$$

Notice that the commutators $[H, \xi^+ q] = +\lambda_q\,\xi_q^+$ and $[H, \xi_q] = -\lambda_q\,\xi_q$ enable us to interpret ξ_q^+ and ξ_q as creation and annihilation operators acting on right and left vacuum (steady) states $|\psi\rangle$, $\langle\tilde{\psi}|$ such that $\xi_q|\psi\rangle = 0$ and $\langle\tilde{\psi}|\xi_q^+ = 0$, whereas the elementary excitations $\xi_q^+|\psi\rangle$ are related to eigenmodes decaying with a characteristic lifetime $\tau_q = (b - a\cos q)^{-1} > 0$. For $\epsilon, \epsilon' \neq 0$ the spectrum of H already signals the fast (exponential) nature of the asymptotic dynamics. In the limit $N \to \infty$ it exhibits a gap $g = 4\min(\epsilon, \epsilon')$ resulting from the creation of *two* elementary ξ excitations $\xi_{q_0}^+\,\xi_{-q_0}^+|\psi\rangle$ with $q_0 = 0^+$ if $\epsilon < \epsilon'$ or $q_0 = \pi^-$ if $\epsilon > \epsilon'$, as the dynamics preserves the parity of the ξ particles (within a given invariant subspace).

Although the similarity transformation (10) breaks down for vanishing desorption (adsorption) rates ϵ' (ϵ), it should be emphasized that the nonequilibrium density and dynamic correlation functions are *well defined* for $\epsilon' \to 0$ ($\epsilon \to 0$). This will be shown in Sec. III B. Therefore our AD model admits slow (power-law) asymptotic solutions as they are no longer dominated by the existence of the spectrum gap.

III. DYNAMIC CORRELATION FUNCTIONS

In this section we turn to the calculation of dynamic particle-particle nonequilibrium correlation functions. We will consider the case of an initially empty substrate, a common situation within the context of AD processes. As is known [20], there is a simple way to express the time development of any physical operator $\mathcal{A}$. For a given initial state $|\varphi_0\rangle$ the dynamic average of $\langle\mathcal{A}(t)\rangle$ is simply $\langle\mathcal{A}(t)\rangle = \langle\tilde{\psi}|\mathcal{A}e^{-Ht}|\varphi_0\rangle$. Thus the particle-particle *connected* correlations are given by

$$C_{l,m}(t) = G_{l,m}(t) - \rho_l(t)\,\rho_m(t),$$
$$G_{l,m}(t) = \langle\tilde{\psi}|\hat{n}_l\,\hat{n}_m\,e^{-Ht}|\varphi_0\rangle,$$
$$\rho_j(t) = \langle\tilde{\psi}|\hat{n}_j\,e^{-Ht}|\varphi_0\rangle, \tag{13}$$

where $G_{l,m}(t)$ is the joint probability distribution to observe simultaneously a pair of particles at locations l and m (i.e., two-point correlations), whereas $\rho_j(t)$ is the average density of site j. Here, $\hat{n}_j = \sigma_j^+\,\sigma_j^- = C_j^\dagger\,C_j$ denotes the occupation number operator which after inverting Eqs. (8) and (10), in the ξ representation can be rewritten as

$$\hat{n}_j = \frac{1}{N}\sum_{k,k'\in Q} e^{i(k'-k)j}\left[(\cos\theta_k)\,\xi_k^+ - (\sin\theta_k)\,\xi_{-k}\right] \times\left[(\cos\theta_{k'})\,\xi_{k'} - (\sin\theta_{k'})\,\xi_{-k'}^+\right]. \tag{14}$$

From Eq. (8) it is clear that $\sum_{q\in Q}\eta_q^\dagger\,\eta_q = \sum_n C_n^\dagger\,C_n = \sum_n \sigma_n^+\,\sigma_n^- \equiv \mathcal{N}$, i.e., the total number of original particles. Hence the vacuum state of the η fermions coincides with the initially empty lattice configuration. This simple but useful remark along with the inversion of Eq. (10) allows one to construct the initial condition $|\varphi_0\rangle$ as a coherent pair state of the form

$$|\varphi_0\rangle = \prod_{q\in P}\left[1 + (\tan\theta_q)\,\xi_q^+\,\xi_{-q}^+\right]|\psi\rangle. \tag{15}$$

Here, the set P denotes the positive values of $q \in Q$, whereas $\langle\tilde{\psi}|\varphi_0\rangle = 1$, as required by conservation of probability [Eq. (2)]. It can be readily verified that $\eta_q|\varphi_0\rangle \equiv 0\ \forall q \in Q$. Hence, after introducing the parameter $\gamma_q \equiv 2\,\mathrm{Re}\,\lambda_q$, the expansion of $e^{-Ht}|\varphi_0\rangle$ yields

$$e^{-Ht}|\varphi_0\rangle = \left[1 + \sum_n \frac{1}{n!}\sum_{q_1\in P}\cdots\sum_{q_n\in P}\left(\prod_{j=1}^n e^{-\gamma_{q_j}t} \times(\tan\theta_{q_j})\,\xi_{q_j}^+\,\xi_{-q_j}^+\right)\right]|\psi\rangle. \tag{16}$$

Recalling that the occupation number operators (14) involve at most *two* ξ excitations, it follows from Eq. (13) that to determine the evolution of the density and the two-point correlations we are left with the calculation of

$$\rho_j(t) = \langle\tilde{\psi}|\hat{n}_j\left(1 + \sum_{q\in P} e^{-\gamma_q t}(\tan\theta_q)\,\xi_q^+\,\xi_{-q}^+\right)|\psi\rangle, \tag{17}$$

$$G_{l,m}(t) = \langle \tilde{\psi} \,|\, \hat{n}_l \, \hat{n}_m \left(1 + \sum_{q \in P} e^{-\gamma_q t} (\tan\theta_q) \, \xi_q^+ \, \xi_{-q}^+ + \frac{1}{2} \sum_{q,q' \in P} e^{-(\gamma_q + \gamma_{q'}) t} (\tan\theta_q)(\tan\theta_{q'}) \times \xi_q^+ \, \xi_{-q}^+ \, \xi_{q'}^+ \, \xi_{-q'}^+ \right) | \psi \rangle \,. \quad (18)$$

Similarly, many particle correlation functions can be treated by this methodology, though their actual calculation becomes increasingly difficult. However, there is a particular subcase, namely, $\epsilon = \epsilon' = h = h'$, which is amenable to an exact treatment. This will be discussed in Sec. IV.

Note that Eq. (16) entails immediate consequences for instantaneous (equal time) correlation functions. Since the drift velocity $\propto h - h'$ enters neither the form (14) nor (15), it is clear that these functions are *independent* of the bias. Actually, for periodic boundary conditions and translationally invariant initial states $|\phi_0\rangle$ this observation is of general character [21].

A. Exponential decay and subdominant power laws

Using the anticommutative algebra associated with the ξ operators the evaluation of (17) is now straightforward. From Eq. (14) it follows that

$$\langle \tilde{\psi} \,|\, \hat{n}_j = \frac{1}{N} \langle \tilde{\psi} \,| \left[\sum_{k \in Q} \sin^2\theta_k - \sum_{k,k' \in Q} e^{i(k'-k)j} (\sin\theta_k) \times (\cos\theta_{k'}) \, \xi_{-k} \, \xi_{k'} \right] . \quad (19)$$

Hence the evolution of the macroscopic density $\rho_j(t) = \rho(t)$ is then given by

$$\rho(t) = \frac{1}{N} \sum_{q \in Q} (\sin^2\theta_q) \left(1 - e^{-\gamma_q t} \right) . \quad (20)$$

Taking into account the angles θ_q of the Bogoliubov transformation (11), in the limit $N \to \infty$ we get

$$\rho(t) = \rho_s - \frac{2\epsilon}{\pi} \int_0^\pi \frac{e^{-\gamma_q t}}{\gamma_q} (1 + \cos q) \, dq \,, \quad (21)$$

where the steady state coverage ρ_s reduces to

$$\rho_s = \frac{2\epsilon}{\pi} \int_0^\pi \frac{1}{\gamma_q} (1 + \cos q) \, dq = \frac{1}{1 + \sqrt{\epsilon'/\epsilon}} \,. \quad (22)$$

Although the calculation of the two-point correlation functions (18) is a simple matter, in fact it becomes rather lengthy. Here we quote the final results, relegating the calculation details to the Appendix. After introducing the (well defined) integrals

$$\mathcal{F}_n(t) = \frac{2}{\pi} \int_0^\pi \frac{e^{-\gamma_q t}}{\gamma_q} (1 + \cos q) \cos(nq) \, dq \,, \quad (23)$$

$$\mathcal{G}_n(t) = \frac{2}{\pi} \int_0^\pi \frac{e^{-\gamma_q t}}{\gamma_q} \sin q \, \sin(nq) \, dq \,, \quad (24)$$

$$\mathcal{H}_n(t) = \frac{2}{\pi} \int_0^\pi \frac{e^{-\gamma_q t}}{\gamma_q \sin q} (1 + \cos q)^2 \sin(nq) \, dq \,, \quad (25)$$

$(n = 0, 1, 2, \ldots)$ along with the dimensionless parameter

$$\beta = \frac{\sqrt{\epsilon'} - \sqrt{\epsilon}}{\sqrt{\epsilon'} + \sqrt{\epsilon}} \quad (26)$$

for $N \to \infty$ we find that $G_{l,m}(t) = G_n(t)$, $(n = |l - m|)$, can be expressed as the sum of five main translationally invariant terms (see the Appendix), namely,

$$G_n(t) = T_1 + T_2(t) + T_3(n,t) + T_4(n,t) + T_5(n,t) \quad , \quad n \geq 1 \,, \quad (27)$$

where the above contributions are given by the following set of equations:

$$T_1 = \rho_s^2 \quad , \quad T_2(t) = -\rho_s \, \epsilon \, \mathcal{F}_0(t) \,, \quad (28)$$

$$T_3(n,t) = \frac{\epsilon \, \epsilon' \, (1 + \beta^2) \, \beta^{n-1}}{2b \, (1 + \beta)} \times \left[(1 - \beta) \, \mathcal{F}_n(t) - (1 + \beta) \, \mathcal{G}_n(t) \right] , \quad (29)$$

$$T_4(n,t) = \epsilon^2 \left[\mathcal{F}_0^2(t) - \mathcal{F}_n^2(t) - \mathcal{G}_n(t) \, \mathcal{H}_n(t) \right] , \quad (30)$$

$$T_5(n,t) = \frac{\epsilon^2 \, (1 + \beta^2) \, \beta^{n-1}}{2b \, (1 - \beta)} \left[(1 + \beta) \, \mathcal{F}_n(t) + (1 - \beta) \, \mathcal{H}_n(t) \right] - \rho_s \, \epsilon \, \mathcal{F}_0(t) \,. \quad (31)$$

As was stated above, the density and pair correlation functions are independent of the drift velocity introduced by the anisotropic hopping.

We have conducted Monte Carlo simulations to confirm the validity of the theoretical expectations given by Eqs. (21) and (27). The simulation procedure goes as follows. Starting from an empty chain of $N = 10^5$ sites with periodic boundary conditions, attempts at dimer deposition, dimer evaporation, and single-particle hopping at random bonds of the lattice take place according to the microscopic rules described in Sec. II. These mutually exclusive processes, either successful or not, are repeated M times after which we set $t \to t + M/N$, $1 \leq M \leq N$. Results for the density and connected pair correlation functions are illustrated in Fig. 2 after averaging the data over 2×10^4 independent runs for $\epsilon = 1$, $\epsilon' = 0.5$, $h = 1$, and $h' = 0.5$ The agreement with our theoretical results is quite good.

Equations (21) and (27) encompass a variety of subdominant power-law prefactors. In analyzing the asymptotic regime $\epsilon t \gg 1$, it turns out that according to the relative values of ϵ and ϵ' the actual long time behavior is

$$C_n(t) \propto \begin{cases} e^{-4\epsilon t} \, t^{-1/2} \,, & 0 < \epsilon < \epsilon' \,, \\ e^{-4\epsilon t} \, \delta_{n,1} \,, & \epsilon = \epsilon' \neq 0 \,, \\ e^{-4\epsilon' t} \, t^{-3/2} \,, & 0 < \epsilon' < \epsilon \,. \end{cases} \quad (32)$$

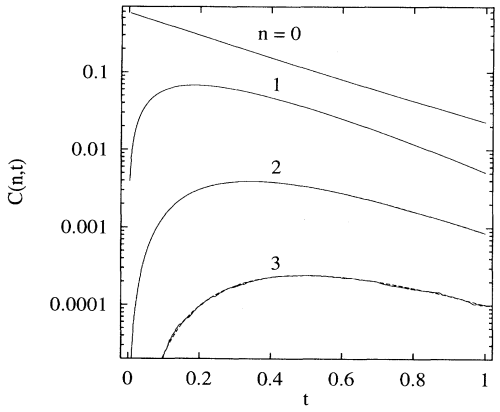

FIG. 2. Connected correlation functions for $\epsilon = 1$, $\epsilon' = 0.5$, and $h = h' = 0.5$. The solid lines denote our numerical results obtained after averaging over 2×10^4 independent histories in a periodic chain of 10^5 sites. The dotted lines (slightly observable at the bottom) are the theoretical values obtained from Eqs. (21) and (27) in the text. The upper curve ($n = 0$) corresponds to the macroscopic density decay.

Identical classification of subdominant power-law exponents arises for the macroscopic density relaxation. This behavior is shown in Figs. 3(a) and 3(b) after integrating numerically Eqs. (23), (24), and (25).

Finally, it is worth remarking here on the constraint $\epsilon + \epsilon' = h + h'$. It turns out to be the condition for our model to be equivalent to a generalized single-spin-flip one-dimensional Glauber dynamics [16] in a description in which kinks $s_j\, s_{j+1}$ (or domain walls) correspond to particle occupation numbers $n_j = (1 - s_j\, s_{j+1})$ [22,13]. However, note that the two-point correlations (27) 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.

B. The limit $\epsilon' \to 0$: Nondiffusive power-law relaxation

As was mentioned in Sec. II, for pure AD ($h = h' = 0$) the Goldstone symmetries (6) give rise to a power-law (diffusive) asymptotic dynamics. In this subsection we show that the case $\epsilon' = 0$, $\epsilon = h + h'$ leads to a slow behavior scenario as well. Due to the initial state of the empty lattice, the adsorption rate must be kept finite ($\epsilon > 0$) since otherwise no dynamics will occur.

After taking the limit $\epsilon' \to 0$ in Eqs. (21) and (27) the evolution of the macroscopic density and the connected pair correlation functions is given by

$$\rho_j(t) = \rho(t) = 1 - e^{-2\epsilon t} I_0(2\epsilon t), \tag{33}$$

$$C_n(t) = -e^{-4\epsilon t} I_n^2(2\epsilon t) - F_n^+(2\epsilon t)\left[(-1)^n + F_n^-(2\epsilon t)\right], \tag{34}$$

where $I_0(z)$ and $I_n(z)$ are the modified Bessel functions of the first kind [24] and

$$F_n^{\pm}(z) = \frac{e^{-z}}{\pi} \int_0^{\pi} \frac{e^{-z\cos q}}{\sin q} \sin(nq)\,(1 \pm \cos q)\, dq\,. \tag{35}$$

We should hasten to add that the validity of this procedure is justified as it is equivalent to taking the limit $\epsilon' \to 0$ *outside* the brackets of Eqs. (17) and (18). Thus neither the Bogoliubov type transformation (10) nor the anticommutative algebra associated with the ξ operators breaks down. Identical results would follow by replacing $\epsilon' \to \epsilon$ starting from an initially full lattice.

In Figs. 4(a) and 4(b) we display respectively our Monte Carlo simulations for the density (along with density fluctuations) and connected pair correlation functions. Setting $\epsilon' \equiv 0$, $\epsilon = 1$, and $h = h' = 0.5$, we have averaged our data over 2×10^3 independent samples starting from an empty chain of 10^5 sites. The agreement with the theoretical results (33) and (34) is remarkable.

For *short* time scales $\epsilon t \ll 1$ it turns out that long range order is negligible, namely, $C_n(t) \propto O(t^{2n})$, $n > 2$. In contrast, within the scaling regime where $n \to \infty$, $\epsilon t \to \infty$ with $n^2/\epsilon t$ held finite, we obtain

$$\rho(t) \simeq 1 - \frac{1}{2\sqrt{\pi \epsilon t}}\,, \quad C_n(t) \simeq -\frac{e^{-\frac{n^2}{2\epsilon t}}}{4\pi\epsilon t} + O(n/t^{3/2})\,. \tag{36}$$

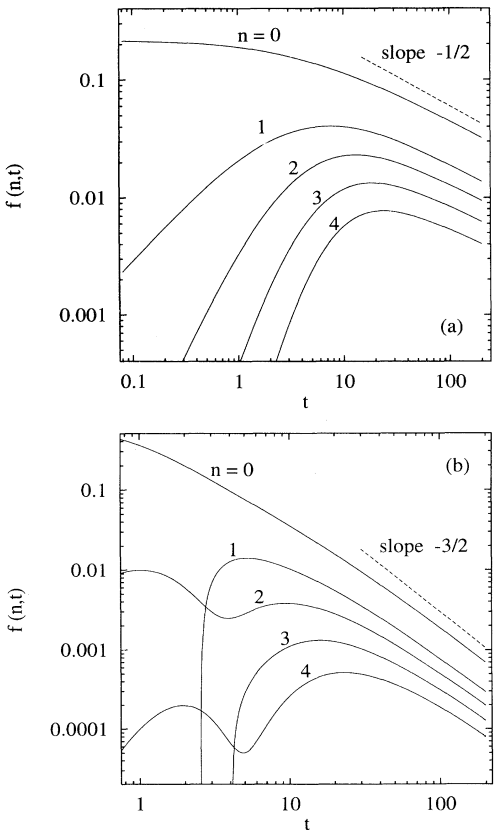

FIG. 3. Subdominant power-law relaxation of pair correlation functions $f(n,t) \equiv C(n,t)\, \exp[4\min(\epsilon, \epsilon')\, t]$ and particle coverage ($n = 0$) by integrating numerically Eqs. (23), (24), and (25) in the text. Results for (a) $\epsilon = 0.03$, $\epsilon' = 0.4$ and (b) $\epsilon = 0.4$, $\epsilon' = 0.03$.

Hence, while the macroscopic density relaxation exhibits the standard diffusive long time tail $\sim t^{-1/2}$, the asymptotic behavior of particle-particle correlations turns out to be anomalous (nondiffusive) in the sense that they decay faster, namely, as t^{-1} [see Fig. 4(b)]. However, notice that according to Eq. (36) their *spreading* is still diffusive. Both features, anomalous decay and diffusive spreading, are shown in Fig. 5. Numerical simulations for $\epsilon \neq h + h'$ strongly indicate that this feature is rather *robust*. Evidence of nondiffusive decay is provided by Fig. 6 where we show results for $\epsilon = 0.7$, $h = 0.6$, and $h' = 0.4$.

It is interesting to understand how such correlations build up a self-similar growth pattern along with the emergence of a diffusive correlation length ξ. From Eq. (36) it is immediate to show that for large times and long wavelengths $\sim q^{-1}$ the nonequilibrium structure factor $S(q,t)$ satisfies time-dependent scaling:

$$S(q,t) = \sum_{n=-\infty}^{+\infty} e^{iqn} C_{|n|}(t) \simeq \mathcal{F}_s(q\,\xi(t))/\xi(t), \qquad n \neq 0, \quad (37)$$

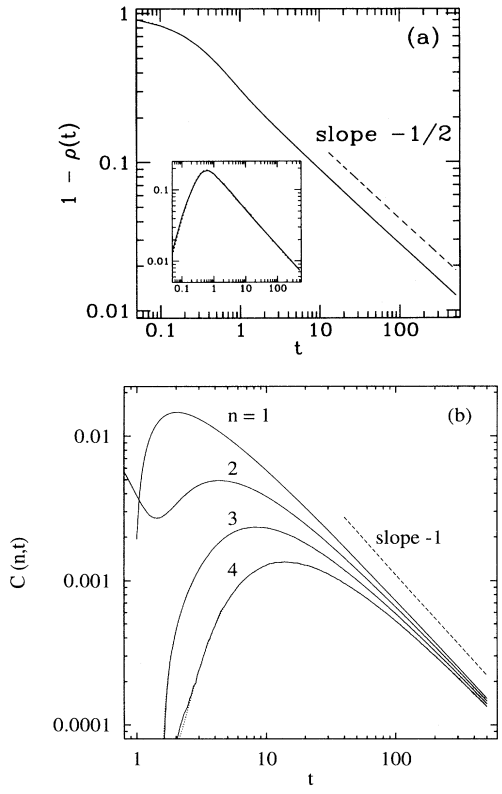

FIG. 4. (a) Diffusive relaxation of particle coverage. The inset at the bottom left displays the evolution of density fluctuations. (b) Nondiffusive decay of equal time connected correlation functions for $\epsilon = 1$, $\epsilon' = 0$, and $h = h' = 0.5$. The averages were taken over 2×10^3 histories starting from an empty lattice of 10^5 sites. The numerical data (solid lines) reproduce entirely the theoretical results given by Eqs. (33) and (34) in the text (dotted lines slightly visible).

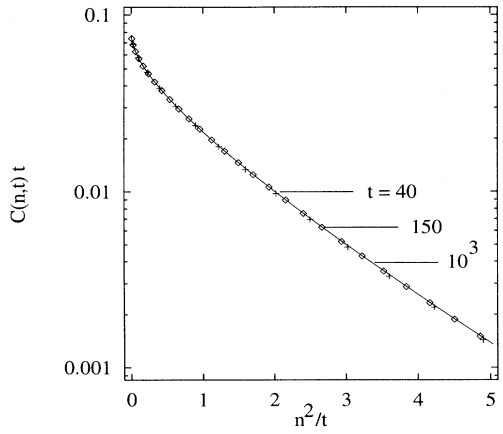

FIG. 5. Scaling behavior of connected correlation functions displaying both diffusive spreading and nondiffusive decay for $t = 40$ (crosses), 150 (squares), and 10^3 (solid line).

with a scaling function $\mathcal{F}_s(z) = -\frac{e^{-z^2/4}}{\sqrt{8\pi}}$ and a correlation length $\xi(t) = (\epsilon t)^{1/2}$. This behavior is illustrated in Fig. 7. In particular, macroscopic density fluctuations $\langle \rho^2(t) \rangle - \langle \rho(t) \rangle = S(0,t) + \rho(t)[1 - \rho(t)]$ decay diffusively as $t^{-1/2}$. This is corroborated by the Monte Carlo simulations shown in Fig. 4(a).

IV. INTERPARTICLE DISTRIBUTION FUNCTIONS

More detailed descriptions of the stochastic dynamics require one in general to consider the analysis of many particle correlations. The interparticle distribution function (IPDF), i.e., the probability of observing two par-

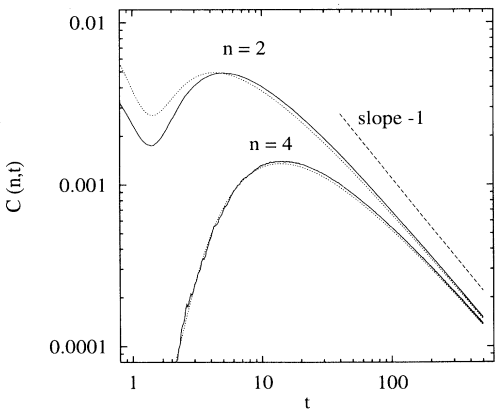

FIG. 6. Numerical evidence of nondiffusive decay for pair correlation functions in the nonsoluble case $\epsilon \neq h + h'$. Our results were averaged over 2×10^3 independent evolution samples of an initially empty chain with 10^5 sites. Solid lines correspond to the case $\epsilon = 0.7$, $\epsilon' = 0$, $h = 0.6$, $h' = 0.4$, whereas the dotted lines represent the theoretical results for $\epsilon = h + h' = 1$. Results for $n = 1$ and 3 are not shown in order to improve the clarity of the figure.

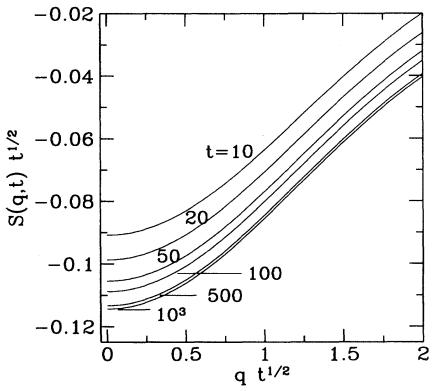

FIG. 7. Time-dependent scaling of nonequilibrium structure factor $S(q,t)$ for large times and long wave-lengths.

ticles separated by a given number of vacancies, is an important example of such correlations and plays a fundamental role in the dynamics of interacting particle systems [1,25]. Specifically, it has been shown that the IPDF determines the early time kinetics of reaction-diffusion models and coagulation systems and achieves a scaling form at long times [26]. Thus it is also of interest to study these distribution functions within the context of our AD systems. The analysis will be limited to the special case $\epsilon = \epsilon' = h = h'$. The calculation scheme presented in Sec. III allows one in principle to obtain many particle correlations for the less restrictive case $\epsilon + \epsilon' = h + h'$; however its implementation becomes quite involved as arbitrary orders of Eq. (16) must be taken into account. We only consider the initially empty lattice configuration since we shall find that for *nonvanishing* AD rates the decay of the IPDF is exponentially fast (as expected), implying that the effect of the initial conditions is only relevant for some short characteristic time.

For $\epsilon = \epsilon' = h = h'$ it is convenient to recast the evolution operator (5) in the Ising form $H = -\epsilon \sum_j \left(\sigma_j^x \sigma_{j+1}^x - 1\right)$. Therefore, due to parity conservation $[H,(-1)^{\mathcal{N}}] = 0$, $(\mathcal{N} = \sum_j n_j^z,\ n_j^z = \sigma_j^+\sigma_j^-)$ and noting that $(-1)^{n^z}\alpha_x = \beta_x$, $(-1)^{n^z}\beta_x = \alpha_x$, the two (normalized) steady states corresponding to each subspace can be constructed as

$$|\psi^{\pm}\rangle = 2^{\frac{N}{2}-1}\left[\prod_k \alpha_x(k) \pm \prod_k \beta_x(k)\right],$$

$$(-1)^{\mathcal{N}} = \pm|\psi^{\pm}\rangle. \quad (38)$$

Since $\alpha_x = (\alpha_z + \beta_z)/\sqrt{2}$ and $\beta_x = (\beta_z - \alpha_z)/\sqrt{2}$, these states represent an equally weighted sum of all reachable configurations with a given parity in the original particle or z representation. Starting from an initially empty chain it is clear that the IPDF $F(k,t)$ or probability of observing two particles located at j_0, j_{k+1}, say, separated by k vacancies on sites $j_1, \ldots, j_k$ $(j_i \equiv j_0 + i)$, remains translationally invariant. Thus the IPDF can be written as

$$F(k,t) = \langle\psi^+|\, n_{j_0}^z \prod_{i=1}^{k}(1-n_{j_i}^z)\, n_{j_{k+1}}^z\, e^{-Ht}\,|\phi_0\rangle. \quad (39)$$

Here, $|\phi_0\rangle = \prod_j \beta_z(j)$ denotes the empty lattice configuration which in turn is given by

$$|\phi_0\rangle = \frac{1}{2^{N/2}} \sum_{\mathcal{S},\mathcal{S}'} \prod_{i\in\mathcal{S}} \alpha_x(i) \prod_{j\in\mathcal{S}'} \beta_x(j), \quad (40)$$

where the sum runs over all possible sets of indices $\mathcal{S},\mathcal{S}'$ such that $\mathcal{S}\cap\mathcal{S}' = \{\emptyset\}$ and $\mathcal{S}\cup\mathcal{S}' = \{1,\ldots,N\}$. Each term of Eq. (40) is an eigenstate of H; hence its contribution to (39) is weighted by a factor $\exp(-2\epsilon N_{\mathcal{S},\mathcal{S}'}t)$, where $N_{\mathcal{S},\mathcal{S}'}$ is the number of kinks or antiparallel nearest-neighbor spins present in each state defined by $\mathcal{S}$ and $\mathcal{S}'$. However, the nonvanishing contributions to $F(k,t)$ are given by those 2^{k+3} configurations of the form

$$\begin{aligned}\{C_A\} &= \{\alpha_x(1)\cdots\alpha_x(j_{-1})\,|\sigma_{j_0}\rangle\cdots|\sigma j_{k+1}\rangle \\ &\quad\times\alpha_x(j_{k+2})\cdots\alpha_x(N)\},\\ \{C_B\} &= \{\beta_x(1)\cdots\beta_x(j_{-1})\,|\sigma_{j_0}\rangle\cdots|\sigma j_{k+1}\rangle \\ &\quad\times\beta_x(j_{k+2})\cdots\beta_x(N)\},\end{aligned} \quad (41)$$

with $|\sigma_n\rangle = \alpha_x(n), \beta_x(n)$, as it is straightforward to show that

$$n_{j_0}^z \prod_{i=1}^{k}(1-n_{j_i}^z)\, n_{j_{k+1}}^z\,|\psi^+\rangle = 2^{\frac{N}{2}-k-3}\left[\prod_{j\neq j_0,\ldots,j_{k+1}}\alpha_x(j) + \prod_{j\neq j_0,\ldots,j_{k+1}}\beta_x(j)\right]$$
$$\times\left[\alpha_x(j_0) - \beta_x(j_0)\right]\prod_{i=1}^{k}\left[\alpha_x(j_i) + \beta_x(j_i)\right]\left[\alpha_x(j_{k+1}) - \beta_x(j_{k+1})\right], \quad (42)$$

where we have used $n^z\alpha_x = -n^z\beta_x = (\alpha_x - \beta_x)/2$. Thus, defining the transfer matrix

$$T = \begin{bmatrix} 1 & e^{-2\epsilon t} \\ e^{-2\epsilon t} & 1 \end{bmatrix} \quad (43)$$

and taking into account the effective "fields" acting on sites j_0 and j_{k+1} with the "border matrices"

$$A = e^{-2\epsilon t}\begin{bmatrix} 1 & e^{-2\epsilon t} \\ -1 & -e^{2\epsilon t} \end{bmatrix},$$

$$B = e^{-2\epsilon t}\begin{bmatrix} e^{2\epsilon t} & 1 \\ -e^{-2\epsilon t} & -1 \end{bmatrix}, \quad (44)$$

associated respectively with configurations $\{C_A\}$ and $\{C_B\}$, the IPDF can finally be computed as

$$F(k,t) = 2^{-(k+3)} \times \sum_{|\sigma\rangle,|\sigma'\rangle} \langle \sigma | A\, T^{k-1}\, A^{\dagger} + B\, T^{k-1}\, B^{\dagger} | \sigma' \rangle . \tag{45}$$

After straightforward algebraic manipulations, we obtain

$$F(k,t) = \frac{e^{-(k+3)\,\epsilon t}}{2} \sinh(2\epsilon t) \left[\cosh^{k}(\epsilon t) \sinh(\epsilon t) + \sinh^{k}(\epsilon t) \cosh(\epsilon t) \right] . \tag{46}$$

For small times it can be readily checked that

$$F(k,t) = \begin{cases} 2\,(\epsilon t)^2 - (2\epsilon t)^3 + O(t^4) \;, & k = 1 \\ (\epsilon t)^2 - (k+3)\,(\epsilon t)^3 + O(t^4) \;, & k > 1 \,, \end{cases} \tag{47}$$

whereas in the limit $t \to \infty$ with $k\, e^{-2\epsilon t} \ll 1$ the asymptotic behavior turns out to be

$$F(k,t) = 2^{-(k+2)} \left[1 + \frac{1}{2}\,(k^2 - 3k - 2)\, e^{-4\epsilon t} + O(e^{-8\epsilon t}) \right] , \tag{48}$$

so $F(k,t) - F(k,\infty)$ scales as $\sim 2^{-(k+3)}\, k^2\, e^{-4\epsilon t}$.

Our Monte Carlo results confirm the dynamic behavior predicted by Eq. (46) for $\epsilon = \epsilon' = h = h'$. This is shown in Fig. 8(a) which exhibits the average over 2×10^3 independent runs starting from an empty chain of $N = 10^5$ sites with periodic boundary conditions. The maximum observed in the distribution functions seems to apply to more realistic situations in which the energetic barriers for desorption are much higher than the corresponding adsorption potentials, i.e., $\epsilon' \ll \epsilon$. This is indicated in Fig. 8(b) where we display our numerical simulations for $\epsilon = 1$, $\epsilon' = 0.1$, and $h = h' = 0.5$. However, for low adsorption probability rates ($\epsilon \ll \epsilon'$) the distribution functions monotonically approach equilibrium from *below*. This is illustrated in Fig. 8(c) for $\epsilon = 0.1$, $\epsilon' = 1$, and $h = h' = 0.5$.

To the best of our knowledge no way of solving exactly the general case (arbitrary ϵ, ϵ', h, h') is presently known. However, it is likely that the elementary excitations of the evolution operator have a gap so long as ϵ (or ϵ') is kept finite. Therefore in general the IPDF might be expected to exhibit an exponential asymptotic regime regardless of the initial conditions.

V. DISCUSSION

In summary, an exact treatment has been given for a stochastic model containing adsorption, desorption, and driven diffusion in one dimension. By various spin rotations within the quantum spin description the model can be mapped into a variety of other models including many well-known subcases.

The technique uses a Jordan-Wigner transformation to a fermion system. The solubility depends on the elimination of many body terms by use of a rate relationship. The results obtained with this constraint appear to be robust, from comparisons with Monte Carlo results for the general case. In this respect, notice that for $\epsilon' = 0$ ($\epsilon = 0$) and long time regimes the density of

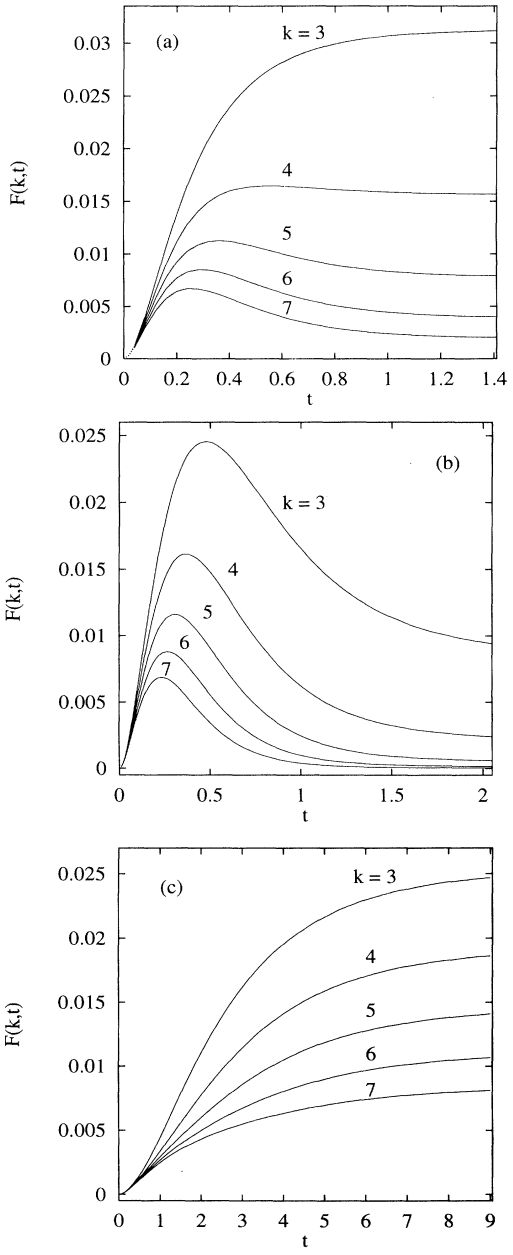

FIG. 8. Interparticle distribution functions obtained by averaging over 2×10^3 independent histories of an initially empty lattice of 10^5 sites. (a) Results for $\epsilon = \epsilon' = h = h' = 1$. The dotted lines (slightly observable at the bottom left) correspond to our theoretical expectations [Eq. (46) in the text] which follow completely the numerical results (solid lines). Results for (b) $\epsilon = 1$, $\epsilon' = 0.1$, $h = h' = 0.5$, and (c) $\epsilon = 0.1$, $\epsilon' = 1$, $h = h' = 0.5$. In all cases the asymptotic values are given by $\rho_s^2\,(1-\rho_s)^k$ with ρ_s as in Eq. (22) in the text.

holes (particles) is rather small and therefore the role of many body terms in (5) becomes irrelevant. The solvable case seems to include all the scenarios seen in the simulations. These scenarios include exponential or power-law asymptotic time dependence, related to a spectral gap or to its disappearance when, for example, desorption is absent ($\epsilon' = 0$). In this gapless case the power-law decay of the pair correlation function has been shown to be faster ($\propto t^{-1}$) than the standard long time tail form ($\propto t^{-1/2}$) seen in the macroscopic density. This is because while the two quantities share the same diffusive dynamics (dynamic exponent $z = 2$) the pair correlation function involves an anomalous superposition of the long wavelength modes. A scaling picture of the asymptotic development of spatial structure has been deduced (for the gapless case). The techniques developed here can in principle be used to calculate n-particle correlation functions for arbitrary n. But this becomes prohibitively complicated for larger n except in the special case with equal rates (and therefore symmetric diffusion) in which the evolution operator is an Ising Hamiltonian. In common with all the analytic results in this paper, these predictions have been confirmed and complemented by Monte Carlo simulations.

The equal time correlation functions calculated in this paper show no dependence on drift $\propto (h - h')$. Unequal time functions discussed elsewhere [23] do contain drift effects (propagating fronts, etc.). Replacing the periodic boundary conditions used here by more general ones (open, possibly with boundary injection processes, reflecting, etc.) is expected to lead to drift effects even in instantaneous correlation functions. This is an interesting extension of the present description which would be most valuable. For more completeness and for comparisons with experimental results, the calculation of higher order equal time and unequal time correlation functions, structure factors, and scattering functions would be desirable.

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APPENDIX: TWO-POINT CORRELATION FUNCTIONS

The evaluation of particle-particle correlation functions requires one actually to take into account all the contributions encompassed within Eq. (18). The rather large number of terms arises from both the form of the occupation number operators in the ξ representaion [Eq. (14)] and the associated anticommutative algebra. For $l \neq m$ basically this gives rise to five main contributions, namely,

$$G_{l,m}(t) = T_1 + T_2 + T_3 + T_4 + T_5 . \tag{A1}$$

Below we address each term in turn. The contribution of T_1 is given by

$$T_1 = \frac{1}{N^2} \langle \tilde{\psi} \mid \sum_{k \in Q} \sin^2 \theta_k \mid \psi \rangle . \tag{A2}$$

Thus, from Eq. (20) if follows that $T_1 = \rho_s^2$. For $k_1 \neq -k_2$ the form of the second term in (A1) can be written as

$$T_2 = -\frac{\rho_s}{N} \sum_{k_1 \in Q} \sum_{k_2 \in Q} \sum_{q \in P} e^{i(k_2 - k_1)m} (\sin\theta_{k_1})(\cos\theta_{k_2}) \times (\tan\theta_q)\, e^{-\gamma_q t} \langle \tilde{\psi} \mid \xi_{-k_1} \xi_{k_2} \xi_q^+ \xi_{-q}^+ \mid \psi \rangle . \tag{A3}$$

Using that

$$\langle \tilde{\psi} \mid \xi_{-k_1} \xi_{k_2} \xi_q^+ \xi_{-q}^+ \mid \psi \rangle = \delta_{k_1,q}\, \delta_{k_2,q} - \delta_{-k_1,q}\, \delta_{-k_2,q} , \tag{A4}$$

it follows that $k_1 = k_2 = q \in Q$. Hence we obtain

$$T_2 = -\frac{\rho_s}{N} \sum_{q \in Q} (\sin^2 \theta_q)\, e^{-\gamma_q t} . \tag{A5}$$

The contribution of T_3 to (A1) is given by the expansion

$$T_3 = -\frac{1}{N^2} \sum_{k_1 \in Q} \cdots \sum_{k_4 \in Q} \sum_{q \in P} e^{i[(k_2 - k_1)l + (k_4 - k_3)m]} \times (\sin\theta_{k_1})(\cos\theta_{k_2})(\cos\theta_{k_3})(\cos\theta_{k_4}) \times (\tan\theta_q)\, e^{-\gamma_q t} \langle \tilde{\psi} \mid \xi_{-k_1} \xi_{k_2} \xi_{k_3}^+ \xi_{k_4} \xi_q^+ \xi_{-q}^+ \mid \psi \rangle , \tag{A6}$$

where $k_1 \neq -k_2$. Noting that the anticommutative algebra yields

$$\langle \tilde{\psi} \mid \xi_{-k_1} \xi_{k_2} \xi_{k_3}^+ \xi_{k_4} \xi_q^+ \xi_{-q}^+ \mid \psi \rangle = \delta_{k_2,k_3} (\delta_{k_1,q}\, \delta_{k_4,q} - \delta_{-k_1,q}\, \delta_{-k_4,q}) - \delta_{-k_1,k_3} (\delta_{-k_2,q}\, \delta_{k_4,q} - \delta_{k_2,q}\, \delta_{-k_4,q}) , \tag{A7}$$

T_3 can be rewritten as

$$T_3 = -\frac{1}{N^2} \sum_{k,q \in Q} \cos[k(l-m)]\, (\cos^2\theta_k)\, \cos[q(l-m)] (\sin^2\theta_q)\, e^{-\gamma_q t} - \frac{1}{N^2} \sum_{k,q \in Q} \sin[k(l-m)]\, (\sin\theta_k)(\cos\theta_k)\, \sin[q(l-m)]\, (\sin\theta_q)(\cos\theta_q)\, e^{-\gamma_q t} , \tag{A8}$$

where we used $\theta_k = -\theta_{-k}$.

The evaluation of the fourth contribution T_4 is straightforward, albeit in fact rather lengthy. It requires the calculation of

$$T_4 = \frac{1}{2N^2} \sum_{k_1 \in Q} \cdots \sum_{k_4 \in Q} \sum_{q,q' \in P} e^{i[(k_2-k_1)l + (k_4-k_3)m]} (\sin\theta_{k_1})(\cos\theta_{k_2})(\sin\theta_{k_3})(\cos\theta_{k_4}) \times (\tan\theta_q)(\tan\theta_{q'})\, e^{-(\gamma_q+\gamma_{q'})t} \langle \tilde{\psi} \,|\, \xi_{-k_1}\xi_{k_2}\xi_{-k_3}\xi_{k_4}\xi_q^+\xi_{-q}^+\xi_{q'}^+\xi_{-q'}^+ \,|\, \psi \rangle . \tag{A9}$$

For $k_1 \neq -k_2, k_3, -k_4$, $k_2 \neq -k_3, k_4$, $k_3 \neq k_4$; and $q \neq q'$, the expansion of $\langle\,\rangle_8$, namely, the eight ξ fermion product evaluated between the left and right steady (vacuum) states, is given by

$$\begin{aligned}\langle\,\rangle_8 = {} & (\delta_{k_1,q'}\delta_{k_2,q'} - \delta_{-k_1,q'}\delta_{-k_2,q'})(\delta_{k_3,q}\delta_{k_4,q} - \delta_{-k_3,q}\delta_{-k_4,q}) \\ & + (\delta_{k_1,q'}\delta_{-k_3,q'} - \delta_{-k_1,q'}\delta_{k_3,q'})(\delta_{k_2,q}\delta_{-k_4,q} - \delta_{-k_2,q}\delta_{k_4,q}) \\ & + (\delta_{-k_2,q'}\delta_{-k_3,q'} - \delta_{k_2,q'}\delta_{k_3,q'})(\delta_{k_1,q}\delta_{k_4,q} - \delta_{-k_1,q}\delta_{-k_4,q}) \\ & + (\delta_{k_1,q'}\delta_{k_4,q'} - \delta_{-k_1,q'}\delta_{-k_4,q'})(\delta_{-k_2,q}\delta_{-k_3,q} - \delta_{k_2,q}\delta_{k_3,q}) \\ & + (\delta_{-k_2,q'}\delta_{k_4,q'} - \delta_{k_2,q'}\delta_{-k_4,q'})(\delta_{-k_1,q}\delta_{k_3,q} - \delta_{k_1,q}\delta_{-k_3,q}) \\ & + (\delta_{k_3,q'}\delta_{k_4,q'} - \delta_{-k_3,q'}\delta_{-k_4,q'})(\delta_{k_1,q}\delta_{k_2,q} - \delta_{-k_1,q}\delta_{-k_2,q}) . \end{aligned} \tag{A10}$$

After collecting the contribution of these terms we obtain the result that T_4 turns out to be

$$\begin{aligned} T_4 = {} & \frac{4}{N^2} \sum_{q,q' \in P} \{1 - \cos[q(l-m)]\cos[q'(l-m)]\}(\sin^2\theta_q)(\sin^2\theta_{q'})\, e^{-(\gamma_q+\gamma_{q'})t} \\ & - \frac{4}{N^2} \sum_{q,q' \in P} \sin[q(l-m)]\sin[q'(l-m)](\sin^2\theta_q)(\tan\theta_q)(\sin\theta_{q'})(\cos\theta_{q'})\, e^{-(\gamma_q+\gamma_{q'})t} . \end{aligned} \tag{A11}$$

Finally, the last term of (A1) reads

$$T_5 = -\frac{1}{N^2} \sum_{k_1 \in Q} \cdots \sum_{k_4 \in Q} \sum_{q \in P} e^{i[(k_2-k_1)l + (k_4-k_3)m]} (\sin\theta_{k_1})(\cos\theta_{k_2})(\sin\theta_{k_3})(\sin\theta_{k_4}) \times (\tan\theta_q)\, e^{-\gamma_q t} \langle \tilde{\psi} \,|\, \xi_{-k_1}\xi_{k_2}\xi_{-k_3}\xi_{-k_4}^+\xi_q^+\xi_{-q}^+ \,|\, \psi \rangle . \tag{A12}$$

For $k_1 \neq -k_2, k_3$, $k_2 \neq -k_3$, the product of the six ξ operators between brackets can be expanded as

$$\begin{aligned} \langle \tilde{\psi} \,|\, \xi_{-k_1}\xi_{k_2}\xi_{-k_3}\xi_{-k_4}^+\xi_q^+\xi_{-q}^+ \,|\, \psi \rangle = {} & \delta_{k_3,k_4}(\delta_{k_2,q}\delta_{k_1,q} - \delta_{-k_2,q}\delta_{-k_1,q}) \\ & - \delta_{-k_2,k_4}(\delta_{k_1,q}\delta_{-k_3,q} - \delta_{-k_1,q}\delta_{k_3,q}) + \delta_{k_1,k_4}(\delta_{-k_3,q}\delta_{-k_2,q} - \delta_{k_2,q}\delta_{k_3,q}) , \end{aligned} \tag{A13}$$

Therefore the contribution of T_5 yields

$$\begin{aligned} T_5 = {} & T_2 + \frac{4}{N^2} \sum_{k,q \in P} \sin[k(l-m)](\sin\theta_k)(\cos\theta_k)\ \sin[q(l-m)](\sin^2\theta_q)(\tan\theta_q)\, e^{-\gamma_q t} \\ & + \frac{4}{N^2} \sum_{k,q \in P} \cos[k(l-m)](\sin^2\theta_k)\ \cos[q(l-m)](\sin^2\theta_q)\, e^{-\gamma_q t} . \end{aligned} \tag{A14}$$

Taking into account the angles θ_q of the Bogoliubov transformation (10) and after introducing the quadratures [24]

$$\frac{1}{\pi}\int_0^\pi \frac{\cos(nq)(1 \pm \cos q)}{b - a\cos q}\, dq = \pm \frac{(1+\beta^2)(1 \pm \beta)}{2b(1 \mp \beta)}\, \beta^{n-1} , \tag{A15}$$

$$\frac{1}{\pi}\int_0^\pi \frac{\sin(nq)\sin q}{b - a\cos q}\, dq = \frac{1+\beta^2}{2b}\, \beta^{n-1} , \tag{A16}$$

with $n \equiv |l-m| \geq 1$ and a, b, β taken as in Eqs. (4) and (26), we are now able to evaluate the two-point correlation functions (27). In the limit $N \to \infty$ we finally obtain Eqs. (28)–(31) and therefore $G_n(t)$.

For $m = l$ there is another (sixth) term to consider, namely,

$$\begin{aligned} T_6 = {} & \frac{1}{N^2} \sum_{k_1 \in Q} \cdots \sum_{k_4 \in Q} e^{i[(k_2-k_1)l + (k_4-k_3)m]} \\ & \times (\sin\theta_{k_1})(\cos\theta_{k_2})(\cos\theta_{k_3})(\sin\theta_{k_4}) \\ & \times \langle \tilde{\psi} \,|\, \xi_{-k_1}\xi_{k_2}\xi_{k_3}^+\xi_{-k_4}^+ \,|\, \psi \rangle . \end{aligned} \tag{A17}$$

However, using the fact that $\langle \tilde{\psi} \,|\, \xi_{-k_1}\xi_{k_2}\xi_{k_3}^+\xi_{-k_4}^+ \,|\, \psi \rangle = \delta_{k_2,k_3}\delta_{k_1,k_4} - \delta_{-k_1,k_3}\delta_{-k_2,k_4}$ $(k_1 \neq -k_2,\ k_3 \neq -k_4)$, it turns out that T_6 is simply

$$T_6 = \delta_{l,m}\rho_s(1 - \rho_s) . \tag{A18}$$

For this situation it can be verified that $G_{m,m}(t)$ reduces to $\rho_m(t) = \rho(t)$ as it should, where $\rho(t)$ is given by Eq. (21).

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