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Exact solutions for stochastic adsorption-desorption models and catalytic surface processes

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We investigate the stochastic kinetics of adsorption-desorption cooperative processes with single particle biased diffusion. For certain choices of the transition probability rates a quantum spin analogy allows for an exact solution of dynamic correlation functions in the steady state. For nonequilibrium translationally invariant initial conditions, equal-time correlation functions and nonsteady currents are calculated exactly, working from the master equation. Depending on the relative values of the transition rates, these quantities exhibit either power-law decay or exponential decay (with a variety of subdominant power-law prefactors). Our results are compared with Monte Carlo simulations.

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I. INTRODUCTION

This paper provides exact results for a wide class of stochastic systems. The models are especially relevant for adsorption-desorption processes and surface reactions and therefore to catalysis.

Numerical investigations of simple catalysis models [1] have exhibited a rich variety of qualitative behaviors ranging from poisoning to dynamical phase transitions. Previous analytic works have given some understanding of such behavior.

In particular, dimer deposition models [2] show poisoning, through the occurrence of jammed states. These are states which through "exclusion" (forbidden double occupancy of any site) cannot evolve further, even though some sites may be empty. Flory [3] predicted the phenomenon, and succeeded in exactly enumerating the jammed states.

Exact results have been obtained [4] for the dynamics of diffusing hard core particles (i.e., with exclusion), for symmetric diffusion. Vertex model descriptions and Bethe ansatz solutions have also been provided [5] for the asymmetric case which has different rates h and h' for moving to left or right. There has also been great progress recently from Derrida and co-workers [6], utilizing a variety of methods allowing exact calculation of steady-state correlation functions.

Recently, models with evaporation as well as deposition of k-mers have been studied [7,8]. Here k-mers refers to dimers or trimers, etc., for $k = 2, 3$, etc. It was found possible to exactly enumerate the jammed states and to treat exactly the dynamics near particular nearly jammed states. In addition exact solutions were given for dimers, when the rates ϵ and ϵ' for deposition and evaporation are equal ($\epsilon = \epsilon'$). This advance was achieved with the use of a (pseudo)spin description, where spin up or down at site $\mathbf{r}$ corresponds to particle or vacancy at that site. The stochastic evolution process covered by the master equation is then equivalent to the action of a quantum spin Hamiltonian which involves k-spin interaction terms in general. For the dimer case with equal rates ($k = 2$, $\epsilon = \epsilon'$) this Hamiltonian can be mapped into that for the isotropic Heisenberg model. The steady states of the stochastic system correspond to the (known) ground states of the Heisenberg model. Because of the rotation symmetry it turns out to be possible to find the density-density time-dependent correlation functions in the steady state [7,8]. The model just described contains no explicit particle diffusion on the surface. But reconstitution of dimers is allowed for (i.e., any adjacent pair of atoms may evaporate, whether or not they arrived together). This results in diffusive characteristics, so long-time tails occur, as in the diffusion-with-exclusion systems [4].

All these results are generalized in the present paper. Here we study a class of more realistic models of adsorption-desorption processes and catalytic surface reactions which allows both for deposition and evaporation of dimers, in general with different rates ϵ, ϵ', and for explicit asymmetric diffusion of particles on the surface, with rates h, h'. The parameters $(\epsilon, \epsilon', h, h')$ thus label the particular system. The exact solutions previously obtained correspond to $(\epsilon, \epsilon, 0, 0)$, $(0, 0, h, h)$. These cases can be shown to be related by sublattice mappings. In the present paper, we provide exact results for the systems with $(\epsilon, \epsilon', h, h')$ provided (i) $\epsilon = \epsilon'$, $h = h'$ or (ii) $\epsilon + \epsilon' = h + h'$. The quantities found exactly are the steady-state and time-dependent density, the time-dependent correlation functions in the steady state, and the equal-time correlation functions. In the asymmetric case (ii) the particle current is also of interest, and is obtained here.

We should emphasize that although our model has four parameters $(\epsilon, \epsilon', h, h')$ representing dimer deposition and evaporation after recombination and particle diffusion, there are potentially more processes which may be included if one is to have a realistic model of surface catalysis. However, we argue that restricting ourselves to the above parameter space is useful since it allows a complete analytic treatment (as we shall see below), and provides a starting point for generalizations, such as addition of

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monomer evaporation processes. The results include signatures (fast or slow relaxation, etc.) of specific processes included which in principle allow a test of the model by comparing our results to those of experiment and more realistic computer simulations.

The investigation uses a variety of different approaches each specially tailored to the case or quantity being studied. We outline these below, both to explain how they simplify the description of a specific situation and to indicate the structure they impose on the paper.

The main distinction between techniques is in the use (or not) of the quantum spin Hamiltonian. This Hamiltonian is derived in Sec. II (following a description of the basic master equation). It turns out to be convenient for the treatment of the time-dependent density-density correlation functions in the steady state. For the case (i) $\epsilon = \epsilon'$, $h = h'$, treated in Sec. III, a sublattice mapping takes the Hamiltonian to that for the XXZ ferromagnet. This has two (Ising) ground states, so there are correspondingly only two steady states. The calculation of correlation functions in the steady state only requires the single spin-wave excitations from these ground states. So the calculation is tractable for any dimension and, because of the spin-wave gap, leads to exponential asymptotic time decay of density-density correlations together with a subdominant power-law factor. The second case (ii), $\epsilon + \epsilon' = h + h'$, is discussed in Sec. IV. Here the many-body terms disappear from the Hamiltonian, which is now not Hermitian. So a Jordan-Wigner transformation [9] makes it bilinear in fermion operators. A generalized similarity transformation of Bogoliubov type [10] then allows its diagonalization, taking it to a free fermion form. This allows the density and correlation functions of the steady state to be determined (and also in principle the nonequilibrium equal-time correlations but that is much more conveniently and generally treated by another procedure outlined below). Because of the Jordan-Wigner transformation, the solution is limited to the one-dimensional case.

The parts of the paper dealing with equal-time correlation functions use the master equation in various ways. The description does not require that the system has entered the steady-state regime, but it is limited to one dimension. Since this is the first time the equal-time correlation function has been calculated for any deposition-evaporation system it is first discussed in Sec. V for the case without explicit diffusion ($h = h' = 0$). The master equation can be used to obtain a set of equations of motion for the two-point equal-time correlation functions. For the case $\epsilon = \epsilon'$ these equations are closed, allowing exact solutions (Sec. V A). These include the influence of the initial conditions on the subsequent relaxation. Long-range random initial correlations are shown to lead to nondiffusive power-law factors, and implications for the interface roughening models are described. For unequal rates (Sec. V B), a perturbation expansion in $(\epsilon - \epsilon')$ shows that the density has a power-law decay, in contrast to the equal rate case where its decay is exponential for translationally invariant initial conditions. When particle diffusion is added, the set of equations for the correlation functions is again closed provided $\epsilon = \epsilon'$ and $h = h'$ [case (i)], again allowing a full solution (Sec. VI A). Case (ii) (i.e., $\epsilon+\epsilon' = h+h'$) turns out (Sec. VI B) to be the condition for the process to be equivalent to a generalized single spin flip Glauber dynamics in a description in which domain walls correspond to particles. This allows calculation of the density, the equal-time nearest-neighbor correlation function, and the particle current.

The remaining technique used in this investigation is simulation. This has been used to confirm all the principal results of this paper, and to indicate the generic character of the power-law decay of the density and equal-time correlation functions, obtained in Sec. V B by the perturbation method. The simulation results accompany the corresponding analytic ones in their particular sections of the paper.

A general discussion concludes the paper in Sec. VII.

II. MASTER EQUATION AND RELATED SPIN MODELS

In this section we describe the details of the basic processes taken into account by the master equation. We then construct the pseudospin description and its associated quantum Hamiltonian.

Let us consider a d-dimensional lattice on which the basic stochastic steps are deposition and evaporation of dimers along with biased particle hopping. Deposition attempts at random selected locations take place with rate ϵ and are successful only if the two selected nearest-neighbor sites are vacant, i.e., double occupancy is forbidden. Also, evaporation of two randomly selected adjacent particles occurs with rate ϵ'. Additionally, hard core particles hop on the lattice with biased rates. Specifically, if $\vec{\delta}$ denotes one of the basis vectors of the unit cell, a particle at site $\mathbf{r}$ $(\mathbf{r} + \vec{\delta})$ hops with rate h (h') provided the site $\mathbf{r} + \vec{\delta}$ $(\mathbf{r})$ is vacant. The rule of evaporation along with the particle hopping give rise to reconstruction of dimers; thus their identity is not preserved during the deposition-evaporation process. These microscopic dynamical rules are schematized in Fig. 1 for the case of a linear chain. Notice that these processes are mutually exclusive.

The time dependence of this kinetic model is described, as usual, by a master equation which governs the time evolution of the probability distribution. If $P(s,t)$ denotes the probability of finding a configuration $|s\rangle$ at time t and $W(s \to s')$ represents the rate or transition probability per unit time at which configuration $|s\rangle$ evolves to $|s'\rangle$, the master equation is

$$\partial_t P(s,t) = \sum_{s'} \left[W(s' \to s) P(s',t) - W(s \to s') P(s,t) \right] . \tag{1}$$

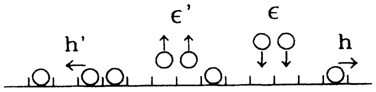

FIG. 1. Schematic description of deposition-evaporation of dimers and biased particle hopping in a linear chain.

The basis vectors $|s\rangle$ are orthonormal and complete, $\langle s|s'\rangle = \delta_{s,s'}$, $\sum_s |s\rangle\langle s| = \mathbf{1}$; hence a state with probability $\{P(s,t)\}_s$ is represented in this space by a vector $|P(t)\rangle$ defined by

$$|P(t)\rangle = \sum_s P(s,t)\,|s\rangle\,. \tag{2}$$

The master equation (1) can now be written as

$$\partial_t\,|P(t)\rangle = -H\,|P(t)\rangle\,, \tag{3}$$

where the operator H is defined in terms of its matrix elements, namely,

$$\begin{aligned} \langle s'|H|s\rangle &= -W(s\to s'),\quad s'\neq s\,,\\ \langle s|H|s\rangle &= \sum_{s'\neq s} W(s\to s')\,. \end{aligned} \tag{4}$$

Thus, formal integration of Eq. (3) defines a stochastic evolution operator e^{-Ht} such that $|P(t)\rangle = e^{-Ht}\,|P(0)\rangle$.

Particles and vacancies of an arbitrary configuration $|s\rangle$ can be denoted by the spinors $\alpha_z = \binom{1}{0}$ and $\beta_z = \binom{0}{1}$, respectively; for instance, in the σ^z representation. Hence, the stochastic dynamics defines a quantum spin-$\frac{1}{2}$ problem via the action of a "Hamiltonian" or evolution operator which we are going to consider and diagonalize for certain choices of the transition rates.

A. The evolution operator

Evidently, through a *single* elementary step the configuration $|s\rangle$ can evolve to $|s'\rangle$ only if $|s\rangle$ differs from $|s'\rangle$ at most by the state of two nearest-neighbor spins at locations $\mathbf{r}$, $\mathbf{r}+\vec{\delta}$, say. The corresponding rates are given by

$$W(s\to s') = \begin{cases} \epsilon\,; & \beta_z(\mathbf{r}),\,\beta_z(\mathbf{r}+\vec{\delta}) \;\to\; \alpha_z(\mathbf{r}),\,\alpha_z(\mathbf{r}+\vec{\delta}),\\ \epsilon'\,; & \alpha_z(\mathbf{r}),\,\alpha_z(\mathbf{r}+\vec{\delta}) \;\to\; \beta_z(\mathbf{r}),\,\beta_z(\mathbf{r}+\vec{\delta}),\\ h\,; & \alpha_z(\mathbf{r}),\,\beta_z(\mathbf{r}+\vec{\delta}) \;\to\; \beta_z(\mathbf{r}),\,\alpha_z(\mathbf{r}+\vec{\delta}),\\ h'\,; & \beta_z(\mathbf{r}),\,\alpha_z(\mathbf{r}+\vec{\delta}) \;\to\; \alpha_z(\mathbf{r}),\,\beta_z(\mathbf{r}+\vec{\delta}). \end{cases} \tag{5}$$

Therefore the nondiagonal part $H_1 = H - \sum_s[\sum_{s'\neq s} W(s\to s')]\,|s\rangle\langle s|$ of the evolution operator H connects states $|s\rangle$ and $|s'\rangle$ through terms of the form

$$\begin{aligned} H_1 = &-\sum_{\mathbf{r},\vec{\delta}}\left(h\sigma^+_{\mathbf{r}+\vec{\delta}}\,\sigma^-_{\mathbf{r}} + h'\sigma^+_{\mathbf{r}}\sigma^-_{\mathbf{r}+\vec{\delta}}\right)\\ &-\epsilon\sum_{\mathbf{r},\vec{\delta}}\sigma^+_{\mathbf{r}}\sigma^+_{\mathbf{r}+\vec{\delta}} - \epsilon'\sum_{\mathbf{r},\vec{\delta}}\sigma^-_{\mathbf{r}}\sigma^-_{\mathbf{r}+\vec{\delta}}, \end{aligned} \tag{6}$$

where $\sigma^+_{\mathbf{r}}$ ($\sigma^-_{\mathbf{r}}$) is a spin-$\frac{1}{2}$ raising (lowering) operator at site $\mathbf{r}$. Let us now consider the diagonal matrix elements of H. From Eq. (4) it is clear that $\langle s|H|s\rangle$ is proportional to the total number of ways in which configurations $|s\rangle$ can evolve to different states $|s'\rangle$ in a *single* elementary step. Therefore, denoting by $n^z_{\mathbf{r}} \equiv \sigma^+_{\mathbf{r}}\sigma^-_{\mathbf{r}}$ the occupation number of site $\mathbf{r}$, the diagonal part $H_2 = \sum_s[\sum_{s'\neq s} W(s\to s')]|s\rangle\langle s|$ of the transition matrix is given by

$$\begin{aligned} H_2 = \sum_{\mathbf{r},\vec{\delta}}\Big[&\epsilon(1-n^z_{\mathbf{r}})\,(1-n^z_{\mathbf{r}+\vec{\delta}}) + \epsilon'\,n^z_{\mathbf{r}}\,n^z_{\mathbf{r}+\vec{\delta}}\\ &+ h\,n^z_{\mathbf{r}}(1-n^z_{\mathbf{r}+\vec{\delta}}) + h' n^z_{\mathbf{r}+\vec{\delta}}(1-n^z_{\mathbf{r}})\Big]\,. \end{aligned} \tag{7}$$

Hence, in terms of the spin-$\frac{1}{2}$ Pauli matrices $\sigma^x_{\mathbf{r}} = \sigma^+_{\mathbf{r}} + \sigma^-_{\mathbf{r}}$, $\sigma^y_{\mathbf{r}} = i(\sigma^-_{\mathbf{r}} - \sigma^+_{\mathbf{r}})$, and $\sigma^z_{\mathbf{r}} = 2\sigma^+_{\mathbf{r}}\sigma^-_{\mathbf{r}} - 1$, the evolution operator $H = H_1 + H_2$ can be finally written as

$$\begin{aligned} H = &\tfrac{1}{2}(\epsilon'-\epsilon)\sum_{\mathbf{r}}\sigma^z_{\mathbf{r}} + \tfrac{1}{4}(\epsilon+\epsilon'-h-h')\sum_{\mathbf{r},\vec{\delta}}\left(\sigma^z_{\mathbf{r}}\sigma^z_{\mathbf{r}+\vec{\delta}} + \sigma^y_{\mathbf{r}}\sigma^y_{\mathbf{r}+\vec{\delta}}\right)\\ &-\tfrac{1}{4}(\epsilon+\epsilon'+h+h')\sum_{\mathbf{r},\vec{\delta}}\left(\sigma^x_{\mathbf{r}}\sigma^x_{\mathbf{r}+\vec{\delta}} - 1\right) + \frac{i}{4}(\epsilon'+h'-\epsilon-h)\sum_{\mathbf{r}\vec{\delta}}\sigma^x_{\mathbf{r}}\sigma^y_{\mathbf{r}+\vec{\delta}}\\ &+\frac{i}{4}(\epsilon'+h-\epsilon-h')\sum_{\mathbf{r}\vec{\delta}}\sigma^y_{\mathbf{r}}\sigma^x_{\mathbf{r}+\vec{\delta}}. \end{aligned} \tag{8}$$

Note that H has a non-negative spectrum because by construction H is a stochastic operator. The steady state of our kinetic model corresponds to the ground state of H with eigenvalue $E_0 = 0$. Eigenvalues E with Re $E > 0$ are related to eigenstates decaying with a lifetime $1/\text{Re}\,E$.

The stochastic dynamics can be solved exactly for the special cases $\epsilon = \epsilon'$, $h = h'$, and $\epsilon + \epsilon' = h + h'$. The first situation corresponds to a uniaxial ferromagnet which, after appropriate spin rotations, can be recast in terms of the XXZ model. Although spin-spin interactions cannot be neglected in this case, it will be shown in Sec. III that the low-lying excitations (i.e., single spin-wave states) are sufficient to yield the correlation functions of the steady state. In one dimension, the second case can be reduced to a free fermion system by means of a Jordan-Wigner transformation followed by a generalized particle-hole or Bogoliubov-type transformation. This will be analyzed in Sec. IV. It is worth pointing out in passing that the free fermion system is directly related to a one-dimensional kinetic Ising model evolving via a generalized single spin flip Glauber dynamics (Sec. VI B) in which particles correspond to kinks or domain walls.

B. Correlation functions in the steady state

In the following sections we will address our attention to the analysis of dynamic correlation functions in the steady state. It is convenient to introduce briefly here some preliminary considerations. Specifically, we are interested in time-dependent particle-particle correlations of the form

$$\langle\, n_{\mathbf{r}'}(t)\, n_{\mathbf{r}}(0)\,\rangle$$

$$\equiv \sum_{s,s'} \langle\, s' \,|\, n_{\mathbf{r}'} \,|\, s' \,\rangle\, W_{s,s'}(t)\, \langle\, s \,|\, n_{\mathbf{r}} \,|\, s \,\rangle\, P(s,0)\ , \quad (9)$$

where $n_{\mathbf{r}}, n_{\mathbf{r}'}$ are occupation number operators at sites $\mathbf{r}$ and $\mathbf{r}'$, respectively, and the sums run over all the possible configurations. Here, $W_{s,s'}(t)$ denotes the evolution probability from state $|s\rangle$ at $t = 0$ to state $|s'\rangle$ at time t, namely $W_{s,s'}(t) = \langle s'|e^{-Ht}|s\rangle$. Assuming that the system is already in equilibrium at $t \geq 0$, $P(s,0)$ characterizes the probability distribution of the steady state $|\,\psi\,\rangle = \sum_s P(s,0)\,|\,s\,\rangle$. Since the number operators $n_{\mathbf{r}}$, $n_{\mathbf{r}'}$ are diagonal in the spin or particle representation $\{|s\rangle\}$, it is clear that $\langle\, s \,|\, n_{\mathbf{r}} \,|\, s \,\rangle\, P(s,0) = \langle\, s \,|\, n_{\mathbf{r}} \,|\, \psi \,\rangle$. Similarly, the *left* steady state $|\,\tilde{\psi}\,\rangle = \sum_s |\,s\,\rangle$ of the evolution operator yields $\langle\, s \,|\, n_{\mathbf{r}} \,|\, s \,\rangle = \langle\, \tilde{\psi} \,|\, n_{\mathbf{r}'} \,|\, s \,\rangle$. Notice that conservation of probability requires $\sum_{s'} \langle\, s' \,|\, e^{-Ht} \,|\, s \,\rangle \equiv 1\ \forall |\, s\,\rangle$ (i.e., every column adds up to 1) and therefore $|\,\tilde{\psi}\,\rangle$ is indeed a left steady state, namely, $\langle\, \tilde{\psi} \,|\, e^{-Ht} = \langle\, \tilde{\psi}\,|$. From the above considerations, it follows immediately that

$$\langle\, n_{\mathbf{r}'}(t)\, n_{\mathbf{r}}(0)\,\rangle = \langle\, \tilde{\psi} \,|\, n_{\mathbf{r}'}\, e^{-Ht}\, n_{\mathbf{r}} \,|\, \psi \,\rangle\,. \quad (10)$$

Thus, if $\{|\,\phi\rangle\}$ and $\{\langle\,\tilde{\phi}\,|\}$ denote respectively a complete set of right and left eigenstates of H, the feasibility of an exact analysis of equilibrium time-dependent correlation functions lies ultimately in the calculation of nonvanishing matrix elements $\langle\, \tilde{\psi} \,|\, n_{\mathbf{r}} \,|\, \phi\,\rangle$, $\langle\, \tilde{\phi} \,|\, n_{\mathbf{r}} \,|\, \psi\,\rangle$ and the knowledge of the ground (steady) state $|\,\psi\,\rangle$.

In general, the correlation functions of nonequilibrium regimes require the expansion of the initial condition in terms of the eigenstates of the evolution operator. In such situations it is more convenient to work directly from the master equation. This will be discussed in Secs. V and VI.

III. THE XXZ FERROMAGNET

In this section we consider the situation where deposition and evaporation rates are the same and the diffusion is symmetric ($\epsilon = \epsilon', h = h'$). In such a case, Eq. (8) simplifies to

$$H = -\frac{\epsilon + h}{2} \sum_{\mathbf{r},\vec{\delta}} \left(\sigma^x_{\mathbf{r}}\, \sigma^x_{\mathbf{r}+\vec{\delta}} - 1 \right) + \frac{\epsilon - h}{2} \sum_{\mathbf{r},\vec{\delta}} \left(\sigma^y_{\mathbf{r}} \sigma^y_{\mathbf{r}+\vec{\delta}} + \sigma^z_{\mathbf{r}} \sigma^z_{\mathbf{r}+\vec{\delta}} \right) . \quad (11)$$

The steady state can be readily obtained by mapping the evolution operator to an XXZ ferromagnet. For $h > \epsilon$ this is produced by the rotation

$$\vec{\tau}_{\mathbf{r}} = U_{\mathbf{r}} \vec{\sigma}_{\mathbf{r}} U_{\mathbf{r}}^{-1}, \quad U_{\mathbf{r}} = \exp\left(i\, \frac{\pi}{4}\, \sigma^y_{\mathbf{r}} \right) ; \quad (12)$$

therefore $\vec{\tau}_{\mathbf{r}} = (\sigma^z_{\mathbf{r}}, \sigma^y_{\mathbf{r}}, -\sigma^x_{\mathbf{r}})$. For *bipartite* lattices $\Lambda = \Lambda_a + \Lambda_b$ (i.e., lattices with nonfrustrated Néel ordering) the case $h < \epsilon$ can also be written as an XXZ ferromagnet through the rotation $\vec{\tau}_{\mathbf{r}} = U_{\mathbf{r}} \vec{\sigma}_{\mathbf{r}} U_{\mathbf{r}}^{-1}$, where

$$U_{\mathbf{r}} = \begin{cases} \exp\left(i \frac{\pi}{4} \sigma^y_{\mathbf{r}}\right) , & \mathbf{r} \in \Lambda_a\,, \\ \exp\left(i \frac{\pi}{2} \sigma^x_{\mathbf{r}}\right)\, \exp\left(i \frac{\pi}{4} \sigma^y_{\mathbf{r}}\right) , & \mathbf{r} \in \Lambda_b\,, \end{cases} \quad (13)$$

thus $\vec{\tau}_{\mathbf{r}} = (\sigma^z_{\mathbf{r}}, \sigma^y_{\mathbf{r}}, -\sigma^x_{\mathbf{r}})$ if $\mathbf{r} \in \Lambda_a$ and $\vec{\tau}_{\mathbf{r}} = (-\sigma^z_{\mathbf{r}}, -\sigma^y_{\mathbf{r}}, -\sigma^x_{\mathbf{r}})$ if $\mathbf{r} \in \Lambda_b$. Hence, in either case the rotation $U = \prod_{\mathbf{r}} U_{\mathbf{r}}$ takes the evolution operator to the form

$$UHU^{-1} = -\frac{|\epsilon - h|}{2} \sum_{\mathbf{r},\vec{\delta}} \left(\tau^x_{\mathbf{r}} \tau^x_{\mathbf{r}+\delta} + \tau^y_{\mathbf{r}} \tau^y_{\mathbf{r}+\delta} + \Delta \tau^z_{\mathbf{r}} \tau^z_{\mathbf{r}+\delta} \right) , \quad (14)$$

where the anisotropy is $\Delta = (\epsilon + h)/|\epsilon - h| \geq 1$.

For $\epsilon = h$ the diagonalization of (11) is trivial; the ground or steady configurations are the two ferromagnetic states

$$|\, F^+ \,\rangle \equiv \prod_{\mathbf{r}} \alpha_x(\mathbf{r}), \quad |\, F^- \,\rangle \equiv \prod_{\mathbf{r}} \beta_x(\mathbf{r})\,. \quad (15)$$

For *nonvanishing* transition rates ϵ, h ($\epsilon \neq h$), the constraint $\Delta > 1$ ensures that the (only) ground states of UHU^{-1} are the two ferromagnetic configurations diagonal in the τ^z representation. Transforming back with U^{-1} it is clear that $|\, F^+ \,\rangle$ and $|\, F^- \,\rangle$ are still steady states of H.

If either ϵ or h is zero the evolution operator has a full rotational symmetry as it can be reduced to an isotropic Heisenberg ferromagnet. In such a case the breaking of this symmetry by the now highly degenerate ground states of H gives rise to low-lying gapless or Goldstone modes which are ultimately responsible for a slow (diffusive) asymptotic behavior [7,8]. Although for nonzero rates ϵ, h the Hamiltonian (11) still exhibits a continuous rotational symmetry around the x axis, notice that $|\, F^+ \,\rangle$ and $|\, F^- \,\rangle$ do not break this symmetry and therefore the Goldstone theorem does not apply in this case.

Therefore a fast (exponential) asymptotic kinetics might be expected.

Due to the parity conservation $[H,(-1)^{\mathcal{N}}]=0$, $\mathcal{N}\equiv\sum_{\mathbf{r}} n^z_{\mathbf{r}}$, the above ground states can not be reached from any initial configuration. However, noting that

$$(-1)^{n^z}\alpha_x=\beta_x,\ (-1)^{n^z}\beta_x=\alpha_x\,, \tag{16}$$

the two physical (normalized) steady states can be constructed as

$$|\psi^\pm\rangle=\frac{\sqrt{2}}{2}\left(|F^+\rangle\pm|F^-\rangle\right),\ (-1)^{\mathcal{N}}|\psi^\pm\rangle=\pm|\psi^\pm\rangle. \tag{17}$$

Each of these states has therefore a well defined parity of particles in the z representation and these states are the two possible steady configurations for nonvanishing rates ($\Delta>1$) $\epsilon=\epsilon'$, $h=h'$. The equilibrium coverage can be easily calculated noting that

$$n^z_{\mathbf{r}}|\psi^\pm\rangle=\frac{\sqrt{2}}{4}\left\{[\alpha_x(\mathbf{r})-\beta_x(\mathbf{r})]\times\left[\prod_{\mathbf{p}\neq\mathbf{r}}\alpha_x(\mathbf{p})\mp\prod_{\mathbf{p}\neq\mathbf{r}}\beta_x(\mathbf{p})\right]\right\}; \tag{18}$$

thus $\langle\psi^\pm|n^z_{\mathbf{r}}|\psi^\pm\rangle=1/2$. Moreover, in the steady state the equal-time $\mathbf{k}$-point correlation functions $\langle n^z_{\mathbf{r}_1}\cdots n^z_{\mathbf{r}_k}\rangle$ factorize as $\langle n^z_{\mathbf{r}_1}\rangle\cdots\langle n^z_{\mathbf{r}_k}\rangle=1/2^k$ as each successive application of $n^z_{\mathbf{r}_n}$ on the left-hand side of Eq. (18) results in the appearance of a factor $\frac{1}{2}[\alpha_x(\mathbf{r}_n)-\beta_x(\mathbf{r}_n)]$ on the right-hand side. Therefore in equilibrium the system is spatially uncorrelated.

The time-dependent two-point connected correlation functions in the steady state

$$C_{\mathbf{r},\mathbf{r}'}(t)\equiv\langle\psi^\pm|n^z_{\mathbf{r}}e^{-Ht}n^z_{\mathbf{r}'}|\psi^\pm\rangle-\langle n^z_{\mathbf{r}}\rangle\langle n^z_{\mathbf{r}'}\rangle \tag{19}$$

can be expanded as

$$C_{\mathbf{r},\mathbf{r}'}(t)=\sum_{|\varphi^\pm\rangle\neq|\psi^\pm\rangle}\langle\psi^\pm|n^z_{\mathbf{r}}|\varphi^\pm\rangle\langle\varphi^\pm|n^z_{\mathbf{r}'}|\psi^\pm\rangle\times e^{-E_{\varphi^\pm}t}, \tag{20}$$

where the states $|\varphi^\pm\rangle$ are a complete set of eigenstates (with defined parity) and eigenvalues E_φ of H. However, from Eq. (18) it is clear that the only contributing states with nonvanishing matrix elements $\langle\varphi^\pm|n^z_{\mathbf{r}}|\psi^\pm\rangle$ are the *single* spin-wave states $|\varphi^\pm_q\rangle$

$$|\varphi^\pm_q\rangle=\frac{1}{\sqrt{2N}}\sum_{\mathbf{r}}e^{i\mathbf{q}\cdot\mathbf{r}}\times\left[\beta_x(\mathbf{r})\prod_{\mathbf{p}\neq\mathbf{r}}\alpha_x(\mathbf{p})\pm\alpha_x(\mathbf{r})\prod_{\mathbf{p}\neq\mathbf{r}}\beta_x(\mathbf{p})\right] \tag{21}$$

with nonvanishing gap spectrum

$$E_q=2d(\epsilon+h)+2(\epsilon-h)\sum_{j=1}^{d}\cos q_j, \tag{22}$$

where $q_j=2\pi n/L_j$, $0\leq n<L_j$, for a hypercubic lattice with $N=L_1\cdots L_d$ sites. From Eqs. (18) and (21) we easily obtain

$$\langle\varphi^\pm_q|n^z_{\mathbf{r}'}|\psi^\pm\rangle=-\frac{1}{2\sqrt{N}}e^{-i\mathbf{q}\cdot\mathbf{r}'}; \tag{23}$$

therefore $C_{\mathbf{r},\mathbf{r}'}(t)$ can be written as

$$C_{\mathbf{r},\mathbf{r}'}(t)=\frac{1}{4N}\sum_{\mathbf{q}}\cos\left[\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')\right]e^{-E_q t}. \tag{24}$$

In the limit $L_j\to\infty$ the correlation functions of the steady state turn out to be

$$C_{\mathbf{r}-\mathbf{r}'}(t)=\frac{1}{4}\exp[-2d(\epsilon+h)t]\prod_{j=1}^{d}I_{n_j}(2|\epsilon-h|t), \tag{25}$$

where I_{n_j} are the modified Bessel functions of integer order [11] and $(\mathbf{r}-\mathbf{r}')=(n_1,\ldots,n_d)$ (the lattice constant has been taken as unity).

We have carried out Monte Carlo simulations to confirm the main results of this section; for simplicity we restricted consideration to the one-dimensional case. The simulation procedure goes as follows. In the initial stage of the algorithm we choose a configuration of $N/2$ particles randomly distributed in a chain of $N=10^5$ sites with periodic boundary conditions. This is in correspondence with the fact that the steady state is spatially un-

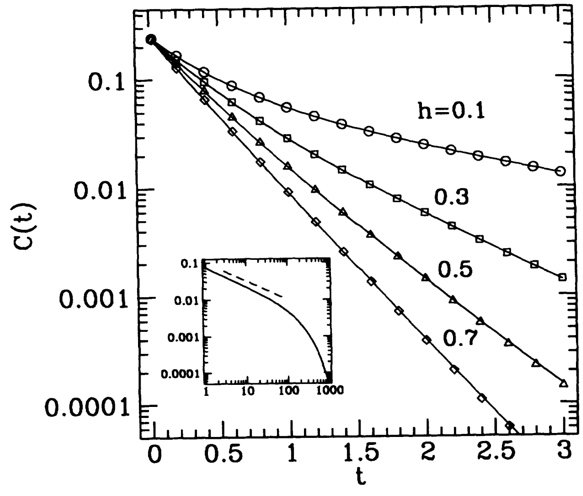

FIG. 2. Autocorrelation function in the steady state for $\epsilon=\epsilon'=1$ and $h=h'$. The open symbols denote the numerical results obtained by averaging over 10^3 samples in a chain of 10^5 sites. The solid lines are the theoretical values [Eq. (25) in the text]. The inset at the bottom left indicates the crossover which results by setting $h=h'=10^{-3}$. The power-law regime is indicated by the dashed line of slope $-1/2$.

correlated and the equilibrium coverage is 1/2. Deposition, evaporation, and hopping attempts are randomly made choosing from the four possible states of the N lattice bonds. These mutually exclusive attempts, either successful or not, are repeated N times after which the time is increased by one unit. Intermediate measurements on time intervals not smaller than $1/N$, of course, can be also attained. We have measured autocorrelation functions by averaging the above procedure on 10^3 samples or histories which turn out to be sufficient to yield an excellent agreement with the theoretical result given by Eq. (25). The simulation results are shown in Fig. 2.

Recalling that $I_n(z) \sim e^z/\sqrt{2\pi z}$ for $z \gg 1$, it follows from Eq. (25) that the autocorrelation functions ($\mathbf{r} = \mathbf{r}'$) in the limit $t \to \infty$ are given by

$$\mathcal{C}(t) \simeq \tfrac{1}{4}\, e^{-t/\tau} \left(4\pi\, |\epsilon - h|\, t \right)^{-d/2} \,, \qquad 1/\tau \equiv 4d \,\min(\epsilon, h) > 0 \,. \tag{26}$$

Hence, for $\tau \gg 1$ there is a crossover regime $\frac{1}{2\,|\epsilon - h|} \ll t \ll \tau$ for which the correlations decay as $\sim t^{-d/2}$. This is illustrated in the inset of Fig. 2.

IV. FREE FERMION MODELS

If we restrict our consideration to the one-dimensional case, in the situation where $\epsilon + \epsilon' = h + h'$ the evolution operator can be reduced to a free fermion Hamiltonian. The cancellation of many-body terms in Eq. (8) yields the following quadratic form:

$$H = -\sum_m \left(h\sigma^+_{m+1}\sigma^-_m \,+\, h'\sigma^+_m\sigma^-_{m+1} \right) - \epsilon \sum_m \left(\sigma^+_m\sigma^+_{m+1} - 1 \right) - \epsilon' \sum_m \sigma^-_m\sigma^-_{m+1} \,-\, (\epsilon - \epsilon') \sum_m \sigma^+_m\sigma^-_m \,. \tag{27}$$

As is well known, in this situation it is convenient to introduce a Wigner-Jordan transformation using fermion operators $C^\dagger_m, C_m$,

$$\sigma^-_m = C_m \,\exp\left(i\pi \sum_{j=1}^{m-1} C^\dagger_j C_j \right) ,$$
$$\sigma^+_m = \exp\left(i\pi \sum_{j=1}^{m-1} C^\dagger_j C_j \right) C^\dagger_m \,. \tag{28}$$

It can be easily checked that $\sigma^+_m\sigma^-_m = C^\dagger_m C_m$, $\forall m$. For $m < N$ we obtain

$$\sigma^+_m\sigma^-_{m+1} = C^\dagger_m C_{m+1}, \quad \sigma^+_m\sigma^+_{m+1} = C^\dagger_m C^\dagger_{m+1} \,, \qquad \sigma^-_m\sigma^-_{m+1} = C_m C_{m+1} \,. \tag{29}$$

For periodic boundary conditions, however, it should be noted that

$$\sigma^+_N\sigma^-_1 = (-1)^{\mathcal{N}+1} C^\dagger_N C_1, \quad \sigma^+_N\sigma^+_1 = (-1)^{\mathcal{N}+1}\, C^\dagger_N\, C^\dagger_1 \,, \qquad \sigma^-_N\sigma^-_1 = (-1)^{\mathcal{N}} C_N C_1 \,, \tag{30}$$

where $\mathcal{N}$ denotes the total particle number operator $\mathcal{N} = \sum_m \sigma^+_m\sigma^-_m = \sum_m C^\dagger_m C_m$.

Since $[H, (-1)^{\mathcal{N}}\,] = 0$ we can split the problem in two subspaces having either even or odd number of particles as was done in Sec. III. For the even subspace we need the anticyclic boundary conditions

$$C_{N+1} = -\,C_1, \quad C^\dagger_{N+1} = -\,C^\dagger_1 \,, \tag{31}$$

while for the odd subspace we use cyclic boundary conditions

$$C_{N+1} = C_1, \quad C^\dagger_{N+1} = C^\dagger_1 \,. \tag{32}$$

To exploit the translational invariance we Fourier transform the fermion operators C_m to the wave fermions η_q

$$\eta^\dagger_q = \frac{1}{\sqrt{N}} \sum_m e^{i\,qm}\, C^\dagger_m \,. \tag{33}$$

To satisfy Eqs. (31) and (32) the wave numbers q should belong respectively to the sets Q^+, Q^- defined as

$$Q^+ = \{\, \pm\pi/N, \pm 3\pi/N, \ldots\,, \pm(N-1)\pi/N \,\} \qquad \text{(even subspace)}\,,$$

$$Q^- = \{\, 0, \pm 2\pi/N, \ldots\,, \pm(N-2)\pi/N, \pi \,\} \qquad \text{(odd subspace)}\,, \tag{34}$$

where we have assumed for convenience that N is even. Using the wave operators η_q it is straightforward to show that $H = \sum_{0 \le q \le \pi} H_q$, where q belongs either to the even or odd set of Eq. (34) and H_q is given by

$$\begin{aligned} H_q &= \omega_q \eta^\dagger_q \eta_q \,+\, \omega^*_q \eta^\dagger_{-q}\eta_{-q} \\ &\quad + 2\sin q \left(\epsilon\eta^\dagger_{-q}\eta^\dagger_q \,+\, \epsilon'\, \eta_q\, \eta_{-q} \right) \,+\, 2\epsilon, \\ \omega_q &= a \,-\, b\,\cos q \,+\, i\,(h' - h)\,\sin q \,, \\ H_0 &= -2\epsilon\eta^\dagger_0\eta_0, \;\; H_\pi = 2\epsilon'\eta^\dagger_\pi\eta_\pi \,. \end{aligned} \tag{35}$$

Here we take $a = \epsilon' - \epsilon$ and $b = \epsilon + \epsilon'$. To diagonalize H_q we introduce here a similarity transformation of Bogoliubov type, namely,

$$\begin{pmatrix} \xi^+_q \\ \xi_{-q} \end{pmatrix} = \begin{pmatrix} \alpha\,\cos\theta_q & \alpha^{-1}\,\sin\theta_q \\ \alpha\,\sin\theta_q & \alpha^{-1}\,\cos\theta_q \end{pmatrix} \begin{pmatrix} \eta^\dagger_q \\ \eta_{-q} \end{pmatrix} \qquad \theta_q = -\,\theta_{-q} \,, \tag{36}$$

where $\alpha = (\epsilon/\epsilon')^{1/4}$, $\theta_0 = 0$, and $\theta_\pi = \pi$. The factor α takes into account the non-Hermitian character of H_q and makes possible its diagonalization using *real* angles

θ_q. Although the transformation (36) is not unitary, it can be easily checked that the operators $\xi_q, \xi_q^\dagger$ are indeed fermion operators, namely, $\left\{\xi_q^+, \xi_{q'}^+\right\}_+ = \{\xi_q, \xi_{q'}\}_+ = 0$ and $\{\xi_q^+, \xi_{q'}\}_+ = \delta_{q,q'}$. However, notice that $\xi_q^+ \neq \xi_q^\dagger$, where † denotes Hermitian conjugation.

After straightforward calculations we found that terms containing operators $\xi_q^+\xi_{-q}^+$ and $\xi_{-q}\xi_q$ can be removed by choosing angles θ_q defined as

$$\tan 2\theta_q = \frac{2\sqrt{\epsilon\epsilon'}\,\sin q}{b\,\cos q - a}\,. \tag{37}$$

Hence, H_q can be cast in the form $H_q = \lambda_q \xi_q^+ \xi_q + \lambda_q^* \xi_{-q}^+ \xi_{-q} - 2\,\epsilon\,\cos q$. Here the elementary (complex) excitation energies are

$$\lambda_q = b - a\,\cos q + i(h' - h)\,\sin q\,. \tag{38}$$

Note that $\mathrm{Re}\,\lambda_q > 0$ as it should correspond to the spectrum of a stochastic evolution operator. Since $[H_q, \xi_q^+]_- = +\lambda_q\xi_q^+$ and $[H_q, \xi_q]_- = -\lambda_q\xi_q$, it is clear that ξ_q^+ and ξ_q can still be interpreted as creation and annihilation operators defined on right and left vacuum states $|\psi\rangle$ and $|\tilde{\psi}\,\rangle$ such that $\xi_q\,|\psi\rangle = 0$ and $\langle\tilde{\psi}\,|\xi_q^+ = 0$.

Parity conservation allows one to create only an even (odd) number of ξ excitations; for simplicity in what follows we discuss the even space situation, although analogous considerations will hold for the odd subspace. Noting that $\lambda_{-q} = \lambda_q^*$ and $\sum_{0<q<\pi}\cos q = 0$, the evolution operator adopts the diagonal form

$$H = \sum_{q \in Q^+} \lambda_q \xi_q^+ \xi_q\,. \tag{39}$$

It follows that the right vacuum $|\psi\rangle$ yields the ground or steady state for the even sector Q^+. Therefore in the limit $N \to \infty$ the spectrum exhibits a gap $g = 4\min(\epsilon, \epsilon')$ resulting from the creation of two excitations $\xi_{-q_0}^+\xi_{q_0}^+\,|\psi\rangle$ with $q_0 = 0^+$ if $\epsilon < \epsilon'$ or $q_0 = \pi^-$ if $\epsilon > \epsilon'$. Thus the asymptotic kinetics for $\epsilon, \epsilon' \neq 0$ turns out to be exponentially fast as it is ultimately dominated by the existence of this gap.

The calculation of dynamic correlation functions in the steady state is now straightforward. First, it is convenient to express the occupation number operators $n_m^z = \sigma_m^+\sigma_m^- = C_m^\dagger C_m$ in terms of the new ξ fermions. Inverting (33) and (36), we obtain

$$C_m^\dagger C_m = \frac{1}{N}\sum_{q,q'} e^{i(q'-q)m}\left(\cos\theta_q\,\xi_q^+ - \sin\theta_q\,\xi_{-q}\right) \times \left(\cos\theta_{q'}\,\xi_{q'} - \sin\theta_{q'}\,\xi_{-q'}^+\right). \tag{40}$$

In particular, the density of particles ρ_m in the steady state at a given site m can be computed as $\langle\tilde{\psi}\,|C_m^\dagger C_m|\,\psi\rangle$. However,

$$C_m^\dagger C_m\,|\psi\rangle = \frac{1}{N}\Big(\sum_q \sin^2\theta_q - \sum_{q,q'} e^{i(q'-q)m}\cos\theta_q\,\sin\theta_{q'}\xi_q^+\xi_{-q'}^+\Big)\,|\psi\rangle\,; \tag{41}$$

hence it follows that in the thermodynamic limit $N \to \infty$

$$\rho_m = \langle\tilde{\psi}\,|C_m^\dagger C_m\,|\psi\rangle = \frac{1}{\pi}\int_0^\pi \sin^2\theta_q\,d_q = \frac{\epsilon}{\pi}\int_0^\pi \frac{1+\cos q}{b - a\,\cos q}\,d_q = \frac{1}{1+\sqrt{\epsilon'/\epsilon}}\,, \tag{42}$$

where we have used $\langle\tilde{\psi}\,|\,\psi\rangle = 1$ as is required by conservation of probability. Similarly, it is straightforward to show that in the equilibrium regime the system is spatially uncorrelated, i.e., $\langle\tilde{\psi}\,|C_{m_1}^\dagger C_{m_1}\cdots C_{m_k}^\dagger C_{m_k}\,|\psi\rangle = \rho_{m_1}\cdots\rho_{m_k} = \rho^k$.

The time-dependent two-point connected correlation functions in the steady state are now computed as

$$\mathcal{C}_{l,m}\,(t) = \langle\tilde{\psi}\,|C_l^\dagger C_l e^{-Ht} C_m^\dagger C_m|\psi\rangle - \rho^2\,. \tag{43}$$

Noting that

$$\langle\tilde{\psi}\,|C_l^\dagger C_l = \frac{1}{N}\langle\tilde{\psi}\,|\Big(\sum_k \sin^2\theta_k - \sum_{k,k'} e^{i(k'-k)l}\sin\theta_k\,\cos\theta_{k'}\,\xi_{-k}\xi_{k'}\Big)\,, \tag{44}$$

and recalling Eq. (41), we obtain

$$\mathcal{C}_{l,m}(t) = \frac{1}{N^2}\sum_{k,k'}\sum_{q,q'} e^{i(k'-k)l}\,e^{i(q'-q)m}\,e^{-(\lambda_q+\lambda_{-q'})t} \times \sin\theta_k\cos\theta_{k'}\,\cos\theta_q\,\sin\theta_{q'} \times\langle\tilde{\psi}\,|\,\xi_{-k}\xi_{k'}\,\xi_q^+\xi_{-q'}^+\,|\psi\rangle\,. \tag{45}$$

Since $\langle\tilde{\psi}\,|\,\psi\rangle = 1$ it is clear that

$$\langle\tilde{\psi}\,|\,\xi_{-k}\xi_{k'}\xi_q^+\xi_{-q'}^+|\psi\rangle = (1-\delta_{-q,q'})\,(1-\delta_{-k,k'}) \times(\,\delta_{k,q'}\delta_{k',q} - \delta_{-k,q}\delta_{-k',q'}\,)\,. \tag{46}$$

Using $\theta_q = -\theta_{-q}$, $\mathrm{Im}\,\lambda_q = -\mathrm{Im}\,\lambda_{-q}$, and Eq. (37), it follows that in the limit $N \to \infty$ the dynamic correlation functions in the steady state can be finally written as

$$\mathcal{C}_{m-l}(t) = \frac{4\,\epsilon\epsilon'}{\pi^2}\left\{\int_0^\pi \frac{e^{-\mathrm{Re}\,\lambda_q t}}{\mathrm{Re}\,\lambda_q}\cos\left[\mathrm{Im}\,\lambda_q t + q\,(m-l)\right]\cos^2\frac{q}{2}\;dq\right\} \times\left\{\int_0^\pi \frac{e^{-\mathrm{Re}\,\lambda_q t}}{\mathrm{Re}\,\lambda_q}\cos\left[\mathrm{Im}\,\lambda_q t + q\,(m-l)\right]\sin^2\frac{q}{2}\;dq\right\} +\frac{\epsilon\epsilon'}{\pi^2}\left\{\int_0^\pi \frac{e^{-\mathrm{Re}\,\lambda_q t}}{\mathrm{Re}\,\lambda_q}\sin\left[\mathrm{Im}\,\lambda_q t + q\,(m-l)\right]\sin q\;dq\right\}^2, \tag{47}$$

where $\mathrm{Re}\,\lambda_q = \epsilon + \epsilon' + (\epsilon - \epsilon')\cos q$ and $\mathrm{Im}\,\lambda_q = (h' - h)\sin q$.

Following the same simulation procedure described at the end of Sec. III, we have computed autocorrelation functions ($m = l$) in the steady state obtaining an excellent agreement with Eq. (47). We direct the reader's attention to Figs. 3(a) and 3(b) where we display respectively our Monte Carlo results for symmetric ($h = h'$) and asymmetric ($h \neq h'$) hopping rates. The averages were taken over 10^3 samples in the steady state of a chain with $N = 10^5$ sites.

For the nonbiased case $h = h'$ it can be checked from Eq. (47) that the autocorrelation function $\mathcal{C}(t)$ exhibits a crossover between two different regimes, namely

$$\mathcal{C}(t) \sim \begin{cases} \sqrt{\frac{\pi^3}{2gt}}\,, & 1 \ll t \ll \tau \\ \frac{2\pi}{g^2}\, e^{-gt}\, t^{-2}\,, & t \gg \tau\,, \end{cases} \tag{48}$$

where $g = 4\min(\epsilon, \epsilon')$ is the gap of the spectrum and $\tau = 2\pi^{-1/3}/g$ is the characteristic crossover time. This behavior is shown in the inset of Fig. 3(a).

Finally, for small times it can be readily shown that the case $h \neq h'$ yields $\mathcal{C}(t) \sim \rho(1-\rho)e^{-t/\tau_0}$, where $\tau_0 = (\sqrt{\epsilon} + \sqrt{\epsilon'})^{-2}$ and ρ is the equilibrium coverage given by Eq. (42).

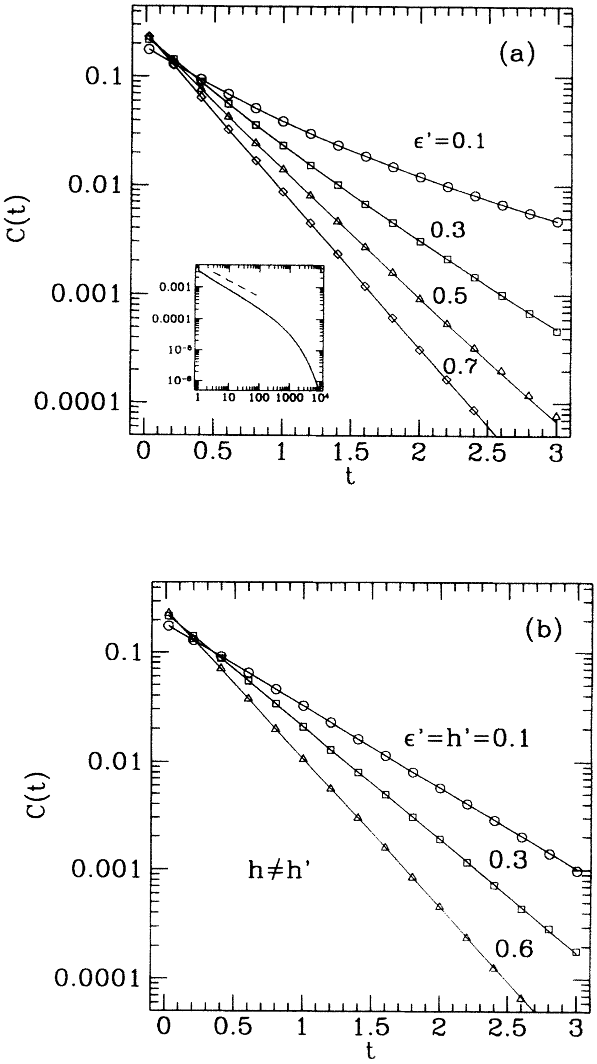

FIG. 3. Autocorrelation function for the case $\epsilon + \epsilon' = h + h'$ with $\epsilon = h = 1$. The data (denoted by the open symbols) were averaged over 10^3 histories in the steady state of a chain with 10^5 sites. (a) Numerical results for the symmetric case $h = h'$. The solid lines are the theoretical values [Eq. (47) in the text]. By setting $\epsilon' = 5 \times 10^{-5}$ a crossover from power law (dashed line of slope $-1/2$) to exponential decay is obtained. This is shown in the inset at the bottom left. (b) Numerical results for the asymmetric case $h \neq h'$. The solid lines are the values resulting from Eq. (47) in the text. The slopes are $-(\sqrt{\epsilon} + \sqrt{\epsilon'})^2 \log_{10} e$.

V. NON-STEADY-STATE PROPERTIES

We have seen the usefulness of the quantum spin representation of the dimer system in evaluating steady-state (SS) properties such as the autocorrelation function. It is also of interest to study the behavior of the system for intermediate times such that the initial preparation of the system is still relevant, and the system has not yet entered the SS regime. In order to study this regime we shall work directly from the master equation. In this section we shall treat the dimer deposition/evaporation problem with no particle diffusion. The effects of particle diffusion on non-SS properties will be studied in the following section.

Let $\{x_i\}$ denote the occupation numbers along the chain. They are restricted in value: $x_i = 0, 1$. For dimer deposition with rate ϵ and evaporation with rate ϵ' we have the following master equation [12] for the distribution function $P(\mathbf{x}, t)$:

$$\begin{aligned} \partial_t P(\mathbf{x}, t) = \frac{1}{2}\sum_i \{&\epsilon[-x_i x_{i+1} P(\mathbf{x}, t) \\ &+(1 - x_i)(1 - x_{i+1})P(\ldots, x_i + 1, x_{i+1} + 1, \ldots; t)] \\ &+\epsilon'[-(1 - x_i)(1 - x_{i+1})P(\mathbf{x}, t) \\ &+x_i x_{i+1} P(\ldots, 1 - x_i, 1 - x_{i+1}, \ldots; t)]\}\,. \end{aligned} \tag{49}$$

In what follows we shall take the initial conditions to be translationally invariant (TI); thus the system will be TI for all subsequent times.

From this equation it is possible to derive equations of motion for the averaged quantities such as the density $\rho(t) = \langle x_i \rangle$ and the two-point equal-time correlation function $c(n,t) = \langle x_i x_{i+n} \rangle$. The angular brackets denote an average over the distribution function P.

For the case of unequal rates $\epsilon \neq \epsilon'$ the equations of motion are not closed—the equation for the two-point function involves the three-point function, and so on. This makes the equations intractable and some other approach is required (see Sec. V B). However, when the rates are equal the equations of motion are closed and we may solve them exactly to find the density and the two-point correlation function.

A. Equal rates

The equations of motion are as follows (we rescale time $t \to t = \epsilon t$ for convenience):

$$\partial_t \rho(t) = 1 - 2\rho(t) \tag{50}$$

and

$$\partial_t c(1,t) = \tfrac{1}{2} - c(1,t) - c(2,t), \tag{51}$$

$$\partial_t c(n,t)|_{n\geq 2} = 2\rho(t) - c(n-1,t) - 2c(n,t) - c(n+1,t), \tag{52}$$

with the conditions $c(n,t) = c(-n,t)$ and $c(0,t) = \rho(t)$.

The solution of (50) is trivial and is given by

$$\rho(t) = \rho(0)e^{-2t} + \tfrac{1}{2}(1 - e^{-2t}). \tag{53}$$

In order to solve Eqs. (51) and (52) it is convenient to Fourier transform in space which enables one to integrate the equations in time. Inverse transforming then yields the following equation for $c(n,t)$:

$$\begin{aligned} c(n,t) = {} & \rho(0)e^{-2t}[I_n(-2t) + 1 - e^{-2t}] + \tfrac{1}{4}(1 - e^{-2t})^2 \\ & + e^{-2t}\sum_{r\neq 0} c(r,0) I_{n-r}(-2t) \\ & + \int_0^t dt'[1 - 2\rho(t') + 2c_1(t')]e^{-2(t-t')} \\ & \times [2I_n(-2(t-t')) + I_{n-1}(-2(t-t')) + I_{n+1}(-2(t-t'))], \end{aligned} \tag{54}$$

where $I_n(z)$ is the modified Bessel function [11].

The functions $c(n,t)$ depend explicitly on the function $c(1,t)$, so we must first determine this function. The simplest way to accomplish this is to set $n = 0$, thus making the left-hand side of (54) equal to the density $\rho(t)$. Laplace transforming the subsequent equation and noting that the integral on the right-hand side is a convolution allows us to algebraically solve for the Laplace transform of $c(1,t)$. Inverse Laplace transforming then gives us the required solution. It is convenient at this point to define the connected two-point correlation functions ($n \neq 0$)

$$b(n,t) \equiv c(n,t) - \rho(t)^2. \tag{55}$$

We then have from the above calculation

$$\begin{aligned} b(1,t) = {} & e^{-2t}[\tfrac{1}{2} - \rho(0)]^2[I_0(2t) - e^{-2t}] \\ & + e^{-2t}\sum_{r=1}^{\infty}(-1)^{r+1} b(r,0) \\ & \times [I_{r-1}(2t) + I_r(2t)]. \end{aligned} \tag{56}$$

Substituting this solution into (54) enables us to find the general function

$$\begin{aligned} b(n,t) = {} & 2(-1)^{n+1}[\tfrac{1}{2} - \rho(0)]^2 \sum_{k=0}^{\infty}(-1)^k I_{n+k}(2t) \\ & + (-1)^n e^{-2t}\sum_{r=1}^{\infty}(-1)^r b(r,0) \\ & \times [I_{n+r-1}(2t) + I_{n-r}(2t)]. \end{aligned} \tag{57}$$

Notice that these solutions are valid for an arbitrary TI initial condition.

We are especially interested in the asymptotically large time behavior of these quantities. First we note from (53) that the density always decays exponentially fast to its SS value. This is unique to the case of equal rates as we shall see later on. Let us now concentrate on the function $b(1,t)$ whose behavior is generic for the functions $b(n,t)$ (so long as n is not very large).

We see from (56) that if the initial density is not equal to its SS value, then the asymptotic decay is of the form $b(1,t) \sim t^{-1/2}$ so long as there are no slower decays arising from the sum over $b(n,0)$. This implies that the approach to the SS is much slower for the two-point functions as compared to the density which relaxes as an exponential. The SS is not reached in a finite time.

If the initial density is equal to the SS value of $\frac{1}{2}$ then the first term in (56) vanishes and the only contribution is from the sum of initial correlators. One can see that this sum has the general asymptotic behavior of diffusion giving again $b(1,t) \sim t^{-1/2}$. There are, however, some special cases. If the initial values are $\rho(0) = \frac{1}{2}$ and $b(n,0) = \frac{1}{4}(-1)^n$ then we find $b(n,t) = b(n,0)$—this is consistent since such an initial condition corresponds to every alternate site occupied—the one frozen state for this system. Also, if the initial values are $\rho(0) = \frac{1}{2}$ and $b(n,0) = 0$ then trivially $b(n,t) = 0$ which is consistent since this initial condition corresponds to the steady state.

We may also generate nondiffusive behavior for the connected functions by defining a distribution of *random* initial conditions. We shall take this distribution to be Gaussian such that it is completely defined by the values of $[\rho(0)]$ and $[b(n,0)]$. Here the square brackets indicate an average over the initial distribution. To generate subdiffusive decay it is necessary to choose the distribution of initial conditions to have power-law tails. Consider the case

$$[b(n,0)] = (-1)^n D/|n|^a. \tag{58}$$

We may evaluate $[b(1,t)]$ by averaging (56) over the initial conditions. The second term is nontrivial to evaluate, but the asymptotic behavior may be extracted. We find

$$[b(1,t)] \sim \begin{cases} -D\frac{\Gamma(1-a)}{\Gamma(1-a/2)}t^{-a/2}, & 0 < a < 1, \\ -D\frac{\ln t}{2(\pi t)^{1/2}}, & a = 1, \\ O(t^{-1/2}), & a > 1, \end{cases} \tag{59}$$

where $\gamma(z)$ is the gamma function. Notice the crossover behavior to diffusive decay when the strength of the long-range initial conditions is reduced: $a > 1$.

Before continuing we pause to consider these results for long-range initial conditions in the context of interface roughening. It is known that there exists a mapping from the (1+1)-dimensional restricted solid-on-solid (RSOS) model (with equal deposition and evaporation rates) to the symmetric exclusion process [13]. This exclusion process actually becomes identical to the dimer problem considered here (with equal rates) under a sublattice mapping—alternate particles (holes) are switched to holes (particles). The implication of this mapping is the following. Consider a RSOS interface with an initial distribution of heights which is Gaussian with correlator

$$[\nabla h(0,0)\nabla h(r,0)] = Dr^{-a}. \tag{60}$$

It is known how to relate the interface width to the function $b(1,t)$ defined above [14]. The relation is

$$\partial_t W(t)^2 = -b(1,t). \tag{61}$$

This then implies the following asymptotic growth for the interface width:

$$W(t) \sim \begin{cases} t^{(2-a)/4}, & 0 < a < 1, \\ t^{1/4}(\ln t)^{1/2}, & a = 1, \\ t^{1/4}, & a > 1. \end{cases} \tag{62}$$

We can see that nondiffusive interface fluctuations are induced by the long-ranged initial conditions unless the power-law tails are too weak ($a > 1$), where we then see a crossover to the usual $t^{1/4}$ growth for the RSOS interface.

B. Unequal rates

As we mentioned before, the case of unequal rates is intractable due to the open hierarchy of equations of motion for the correlation functions. However, we may make some progress by performing perturbation theory, taking the parameter $\epsilon - \epsilon'$ to be small. We shall present results for the density, since the corrections to the two-point functions require evaluation of three-point functions which is a highly nontrivial task. For arbitrary rate constants we have the exact equation of motion for the density:

$$\partial_t \rho(t) = 1 - 2\rho(t) + \Delta c(1,t), \tag{63}$$

where $\Delta = 1-\epsilon'/\epsilon$. Writing $\rho(t) = \rho_0(t)+\Delta\rho_1(t)+O(\Delta^2)$ we find

$$\partial_t \rho_1(t) = -2\rho_1(t) + 2c_0(1,t), \tag{64}$$

where $c_0(1,t)$ is the unperturbed value for $c(1,t)$ (as calculated in the previous subsection). This has the asymptotic form:

$$c_0(1,t) = \tfrac{1}{4} + b_0(1,t), \tag{65}$$

where $b_0(1,t)$ is the unperturbed function given in (56). We therefore see that $\rho_1(t)$ has two contributions for large times. First there is a constant piece (equal to $\frac{1}{8}$), and second there is a power-law contribution from the asymptotic form of the connected correlation function $b(1,t)$. Generally this power-law contribution is diffusive, so that we have the result

$$\rho(t) = \rho_{ss} + A\Delta t^{-1/2} + O(\Delta^2), \tag{66}$$

where A is some constant depending on the initial conditions, and ρ_{ss} is the SS value for the density. If the initial conditions are long ranged as in (58) then the power-law decay of the density will be changed according to Eq. (59). We therefore see that, contrary to the equal rates case, the density has a generic power-law decay to its SS value when the rates are not equal. In the absence of long-ranged initial conditions, this decay is diffusive. We direct the reader to Fig. 4(a) where we show the results of a computer simulation of the dimer problem with unequal rates. The simulation was performed in the same way as explained in the previous section, except that in this case the initial condition was taken to be an empty lattice (instead of the usual steady state). We see that the density has diffusive power-law decay even when the rate constants differ by a factor of 2, implying that this result extends beyond perturbation theory.

Although we have not performed perturbation theory for the two-point functions, numerical simulations suggest that the diffusive power-law decay is unaffected by unequal rates—the corrections only appear in the am-

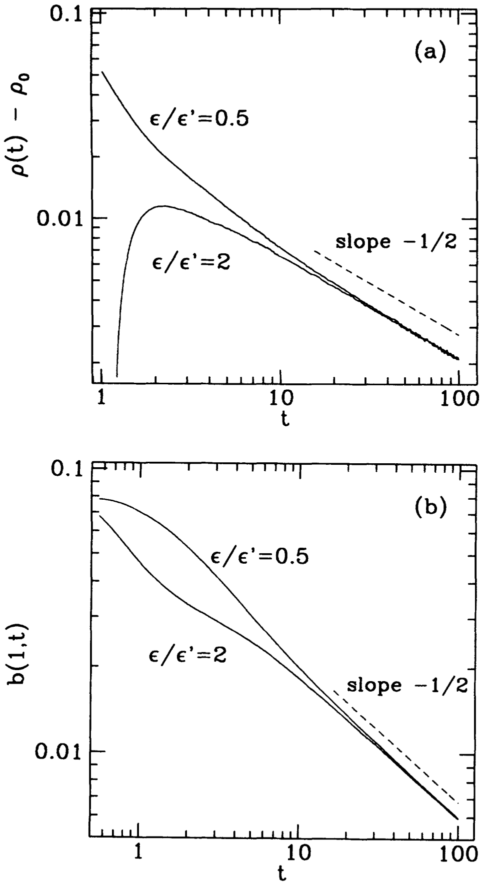

FIG. 4. Evidence of diffusive relaxation in nonequilibrium regimes for $h = h' = 0$ and $\epsilon/\epsilon' = 0.5$, 2. The data were averaged over 10^3 samples starting from an empty chain of 10^5 sites. (a) Numerical results for density deviations from its steady-state value ρ_0 and (b) connected correlation functions $b(1,t)$ referred to in the text.

plitude of the function, but do not affect the dynamic exponent. We refer the reader to Fig. 4(b) where the function $b(1,t)$ is plotted for different ratios of the rate constants.

From the above analysis we may also make a statement concerning mean-field theory. We define mean-field theory (MFT) by decoupling correlation functions into independent density averages. For instance, we approximate $c(n,t) = \rho(t)^2$—equivalently we set the connected function $b(n,t) = 0$. We now ask whether MFT is valid near or in the SS. Referring to Eq. (63), we see that setting $\partial_t\rho(t) = 0$ and using MFT, we can solve exactly for the SS density ρ_{ss}. The solution is

$$\rho_{ss} = \frac{1}{[1 + (\epsilon'/\epsilon)^{1/2}]}, \tag{67}$$

which coincides with the result obtained in [8]. This result is exact since we know that the connected function $b(1,t)$ decays asymptotically to zero, thus making MFT exact in that limit. The fact that this result is exact and yet does not agree with the Flory result for random sequential adsorption ($\epsilon' = 0$) is due to the nonzero asymptote for the connected correlation function in the latter case. If we now shift our attention to large, but finite times we see from (63) in the MFT approximation that the decay of the density will be exponentially fast to its SS value. We know from our perturbation analysis that the decay is actually power law, which immediately implies that MFT is qualitatively wrong for any finite time. It only becomes exact in the strictly infinite time limit when the SS regime is reached.

VI. EFFECTS OF PARTICLE DIFFUSION ON NON-SS PROPERTIES

We now make contact with earlier sections of this paper by considering the effects of (explicit) particle diffusion on the density and two-point correlation functions. In general we may allow for biased hopping with rate h to the left and h' to the right. We therefore have a four-parameter space $(\epsilon, \epsilon', h, h')$ describing our system. We shall see that only special cases in this space allow for an exact solution—these cases being identical to those considered in Secs. III and IV. In the next subsection we consider the case $\epsilon = \epsilon', h = h'$ which gives rise to a set of closed equations for the correlation functions. In the subsequent subsection we consider $\epsilon + \epsilon' = h + h'$ which may be partially solved by a mapping to a Glauber spin system.

A. The case $\epsilon = \epsilon', h = h'$

The case of equal deposition and evaporation rates along with unbiased diffusion turns out to be tractable from the simple master equation approach used in the previous section. The appropriate master equation in this case has the form

$$\begin{aligned}\partial_t P(\mathbf{x},t) = \frac{1}{2}\sum_i \{ &\epsilon[-x_i x_{i+1} P(\mathbf{x},t) + (1-x_i)(1-x_{i+1})P(\ldots, x_i+1, x_{i+1}+1, \ldots; t)] \\ &+\epsilon'[-(1-x_i)(1-x_{i+1})P(\mathbf{x},t) + x_i x_{i+1} P(\ldots, 1-x_i, 1-x_{i+1}, \ldots; t)] \\ &+h[-x_i(1-x_{i-1})P(\mathbf{x},t) + (1-x_i)x_{i-1}P(\ldots, x_{i-1}-1, x_i+1, \ldots; t)] \\ &+h\ [-x_i(1-x_{i+1})P(\mathbf{x},t) + (1-x_i)x_{i+1}P(\ldots, x_i+1, x_{i+1}-1, \ldots; t)]\}.\end{aligned} \tag{68}$$

The equation of motion for the density $\rho(t)$ is unchanged in this case, so the result (53) still holds. The equations for the correlation functions are different however, and are given by

$$\partial_t c(1,t) = \frac{\epsilon}{2} - (\epsilon + h)c(1,t) - (\epsilon - h)c(2,t), \qquad (69)$$

$$\begin{aligned} \partial_t c(n,t)|_{|n|\geq 2} = {} & 2\epsilon\rho(t) - (\epsilon - h)c(n-1,t) \\ & -2(\epsilon + h)c(n,t) \\ & -(\epsilon - h)c(n+1,t) \ . \end{aligned} \qquad (70)$$

We only consider the case of an initially empty lattice since we shall find that the decay of the correlation function is exponentially fast, implying that the effect of the initial conditions is only relevant for some short transient period. The solution of the above equations may be obtained in precisely the same manner as before although the algebra becomes rather heavy (except in the trivial case $\epsilon = h$). We content ourselves with giving just the asymptotic result which takes the form

$$c(n,t) \sim A(n)t^{-1/2} \exp -(h + \epsilon - |h - \epsilon|)t \ , \qquad (71)$$

where $A(n)$ is some constant depending on ϵ and h.

So the effect of particle diffusion is to increase the rate of decay of correlations from some diffusivelike power-law decay to exponentially fast decay. It is interesting to note that the case of pure symmetric hopping ($\epsilon = 0$) has slow power-law decays as with pure dimer deposition/evaporation ($h = 0$)—however the mixture of the two "slow" processes destroys the buildup of correlations in the system with the result that the relaxation to the SS follows exponential decay.

B. The case $\epsilon + \epsilon' = h + h'$

It is well known that certain diffusion-type models may be mapped to the Glauber model [15]—one interprets diffusing particles as domain walls in the Glauber picture. We cite the work of Family and Amar [16] on diffusion annihilation (which corresponds to $\epsilon = 0, h = h'$), and references therein. It turns out that the more general case $\epsilon + \epsilon' = h + h'$ may also be mapped to a Glauber system where now the domain walls have a biased diffusion. We consider Glauber dynamics (i.e. single spin flips $S_i \rightarrow -S_i, S_i = \pm 1$) with a transition probability

$$w(S_i \rightarrow -S_i) = D[1 - \gamma S_i(S_{i-1} + \delta S_{i+1})] \ . \qquad (72)$$

We direct the reader's attention to Fig. 5 where the mapping between particles and domain walls is made clear. The connection between the parameters appearing in the above transition probability and the original parameters $(\epsilon, \epsilon', h, h')$ is of the form

$$\begin{aligned} \epsilon &= D[1 - \gamma(1 + \delta)] \ , \\ \epsilon' &= D[1 + \gamma(1 + \delta)] \ , \\ h &= D[1 - \gamma(1 - \delta)] \ , \\ h' &= D[1 + \gamma(1 - \delta)] \ . \end{aligned} \qquad (73)$$

↑↑↑	↑↓↑	↑↓↓	↑↑↓
↑↓↑	↑↑↑	↑↑↓	↑↓↓
ϵ	ϵ'	h	h'

FIG. 5. Illustrating the mapping between the Glauber spin model and the dimer model. Domain walls in the former correspond to particles in the latter.

Defining $Q(\mathbf{S},t)$ as the probability distribution for the (Glauber) spin configurations, we have the following master equation:

$$\begin{aligned} \partial_t Q(\mathbf{S},t) = D\sum_i \{ & -[1 - \gamma S_i(S_{i-1} + \delta S_{i+1})]Q(\mathbf{S},t) \\ & +[1 + \gamma S_i(S_{i-1} + \delta S_{i+1})] \\ & \times Q(\ldots, -S_i, \ldots; t)\}. \end{aligned} \qquad (74)$$

Defining $f(n,t) = \langle S_i S_{i+n}\rangle_Q$ we may easily derive the following set of equations of motion from (74):

$$\begin{aligned} \partial f(n,t)|_{n\neq 0} = 2D\{ & -2fn, t + \gamma(1 + \delta) \\ & \times[f(n-1,t) + f(n+1,t)]\} \end{aligned} \qquad (75)$$

and $f(0,t) = 1$.

We therefore have a soluble (closed) set of equations for the two-point spin correlation functions. We now note that the original particle occupation numbers are given by $x_i = \frac{1}{2}(1 - S_i S_{i+1})$. Therefore the particle density is given by

$$\rho(t) = \tfrac{1}{2}[1 - f(1,t)] \qquad (76)$$

and the nearest-neighbor particle two-point correlation function is

$$c(1,t) = \tfrac{1}{4}[1 - 2f(1,t) + f(2,t)] \ . \qquad (77)$$

We note that $c(n,t)$ for $n > 1$ requires knowledge of the four-spin correlation functions which is a much more difficult set of functions to calculate.

The solution of (75) may be obtained from the original paper of Glauber (although his original model had symmetric diffusion of domain walls, the equations for the two-spin functions have the same form as those above). We then have

$$\begin{aligned} f(n,t) = \eta^n + e^{-at} & \sum_{l=1}^{\infty}[f(l,0) - \eta^l] \\ & \times[I_{n-l}(bt) - I_{n+l}(bt)] \ , \end{aligned} \qquad (78)$$

where $\eta = 1 - 2\rho_{ss}$, $a = 2(\epsilon + \epsilon')$, and $b = 2(\epsilon' - \epsilon)$.

We shall restrict our attention to the case of an initially empty lattice for simplicity. This corresponds to an initial Glauber spin state of all spins up (or down)—therefore $f(n,0) = 1$. With this initial condition we obtain

$$\rho(t) = \rho_{ss} - \frac{\epsilon}{\pi}e^{-at}\int_0^{\pi} d\theta \frac{(1 + \cos\theta)e^{bt\cos\theta}}{[a - b\cos\theta]} \qquad (79)$$

and

$$c(1,t) = \rho_{ss}^2 - \frac{\epsilon}{\pi} e^{-at} \int_0^{\pi} d\theta \frac{\sin^2\theta e^{bt\cos\theta}}{[a - b\cos\theta]} \ . \tag{80}$$

Since the system has biased diffusion we expect a nonzero current to be present in the system. We define the current $\mathcal{J}$ by

$$\mathcal{J} = \langle h' x_i(1 - x_{i+1}) - h x_{i+1}(1 - x_i)\rangle \ , \tag{81}$$

which is a "staggered current" in the sense that it ignores the effect of dimer deposition/evaporation (in the flux) and simply corresponds to the flux of particles due to the biased diffusion. We have $\mathcal{J} = (h' - h)[\rho(t) - c(1,t)]$ which takes the form

$$\mathcal{J} = (h' - h)\Big\{\rho_{ss}(1 - \rho_{ss}) - \frac{\epsilon}{\pi} e^{-at} \int_0^{\pi} d\theta \frac{\cos\theta(1 + \cos\theta) e^{bt\cos\theta}}{[a - b\cos\theta]}\Big\}. \tag{82}$$

We note that the only effect of the bias is in the prefactor of the current. The bias does not enter the forms of the density or the correlation function $c(1,t)$ as opposed to the situation in the SS where the bias entered the form of the autocorrelation function in a rather complex way.

In analyzing the asymptotic behavior of these quantities it is important to distinguish between certain classes of the relative values of ϵ and ϵ'. There are four such classes which we shall need to discuss. We note that $\epsilon > 0$ always since otherwise no dynamics will occur due to the initial state of the empty lattice.

1. $\epsilon' > \epsilon > 0$

In this case the parameter b is positive. Let us concentrate on the density. Differentiating (79) with respect to time we find

$$\dot\rho(t) = 2\epsilon e^{-at}[I_0(bt) + I_1(bt)] \ . \tag{83}$$

Therefore for large times we have

$$\dot\rho(t) \sim \frac{2\epsilon e^{-4\epsilon t}}{[\pi(\epsilon' - \epsilon)t]^{1/2}} \ . \tag{84}$$

So the asymptotic form of the density is

$$\rho \sim \rho_{ss} - \frac{e^{-4\epsilon t}}{2[\pi(\epsilon' - \epsilon)t]^{1/2}} \ . \tag{85}$$

Using a similar method yields the following result for $c(1,t)$:

$$c(1,t) \sim \rho_{ss} - \frac{e^{-4\epsilon t}}{8\pi^{1/2}[(\epsilon' - \epsilon)t]^{3/2}} \ . \tag{86}$$

We then have for the connected correlation function

$$b(1,t) \sim \frac{\rho_{ss} e^{-4\epsilon t}}{[\pi(\epsilon' - \epsilon)t]^{1/2}} \tag{87}$$

and finally for the density

$$\mathcal{J}(t) \sim (h - h')\left\{\rho_{ss}(1 - \rho_{ss}) - \frac{e^{-4\epsilon t}}{2[\pi(\epsilon' - \epsilon)t]^{1/2}}\right\} \ . \tag{88}$$

So in this case all quantities have exponential decay with power-law prefactors.

2. $\epsilon = \epsilon' \neq 0$

We have $b = 0$ and we find easily from (79), (80), and (82) the following pure exponential behavior:

$$\rho = \tfrac{1}{2}(1 - e^{-4\epsilon t}) \ , \tag{89}$$

$$c(1,t) = \tfrac{1}{4}(1 - e^{-4\epsilon t}) \ , \tag{90}$$

$$b(1,t) = \tfrac{1}{4} e^{-4\epsilon t}(1 - e^{-4\epsilon t}) \ , \tag{91}$$

and finally for the density

$$\mathcal{J}(t) = \frac{(h - h')}{4}(1 - e^{-4\epsilon t}) \ . \tag{92}$$

3. $\epsilon > \epsilon' > 0$

We now have $b < 0$. Following the same steps as in Sec. VI B 2 we find the following results:

$$\rho \sim \rho_{ss} - \left(\frac{\epsilon}{\epsilon'}\right) \frac{e^{-4\epsilon' t}}{16\pi^{1/2}[(\epsilon - \epsilon')t]^{3/2}} \ , \tag{93}$$

$$c(1,t) \sim \rho_{ss} - \left(\frac{\epsilon}{\epsilon'}\right) \frac{e^{-4\epsilon' t}}{8[\pi(\epsilon - \epsilon')t]^{3/2}} \ , \tag{94}$$

$$b(1,t) \sim \frac{(\rho_{ss} - 1)\left(\frac{\epsilon}{\epsilon'}\right) e^{-4\epsilon' t}}{8\pi^{1/2}[(\epsilon - \epsilon')t]^{3/2}} \ , \tag{95}$$

and

$$\mathcal{J}(t) \sim (h - h')\{\rho_{ss}(1 - \rho_{ss}) + \left(\frac{\epsilon}{\epsilon'}\right) \frac{e^{-4\epsilon' t}}{16\pi^{1/2}[(\epsilon - \epsilon')t]^{3/2}}\} \ . \tag{96}$$

It is of interest to note here that the current relaxes to its SS value from above. Initially the current is zero, which implies that the current must pass through a maximum. This is an effect which does not occur for the case of $\epsilon' > \epsilon > 0$. One may intuitively understand this by considering the two contributions to the current—the number of particles and their "mobility". Initially the number of particles rises rapidly and their mobility is essentially constant, therefore the current rises from zero. However, when the density of particles exceeds some critical value the mobility of the particles will start to decrease due to the exclusion effect, thus lowering the value of the current until finally the SS value is reached. In the case where the evaporation rate is greater than the deposition rate (Sec. VI B 1), the density of particles never reaches the critical value and hence the density rises monotonically to its SS value.

4. $\epsilon' = 0$

In this case we have from (79), (80), and (82),

$$\rho(t) = 1 - e^{-2\epsilon t} I_0(2\epsilon t) \sim 1 - \frac{1}{2(\pi \epsilon t)^{1/2}} , \tag{97}$$

$$c(1,t) = 1 - e^{-2\epsilon t}[I_0(2\epsilon t) + I_1(2\epsilon t)] \sim 1 - \frac{1}{(\pi \epsilon t)^{1/2}} , \tag{98}$$

$$b(1,t) \sim -\frac{1}{4\pi \epsilon t} , \tag{99}$$

and

$$\mathcal{J}(t) \sim \frac{(h-h')}{2(\pi \epsilon t)^{1/2}} . \tag{100}$$

In this case we have power-law decay (cf. [16]) for all quantities. Note that the connected correlation function $b(1,t)$ decays faster than the density, i.e., as $1/t$ rather than diffusively. In Fig. 6 we show Monte Carlo results for the functions $b(n,t)$ for some small values of n. All the functions decay as $1/t$. As was mentioned earlier the evaluation of $b(n,t)$ for $n \neq 1$ is highly nontrivial in this case, requiring the evaluation of four-spin correlation functions in the Glauber model. Note also that the current has a maximum—for the same reason as explained in the previous subsection.

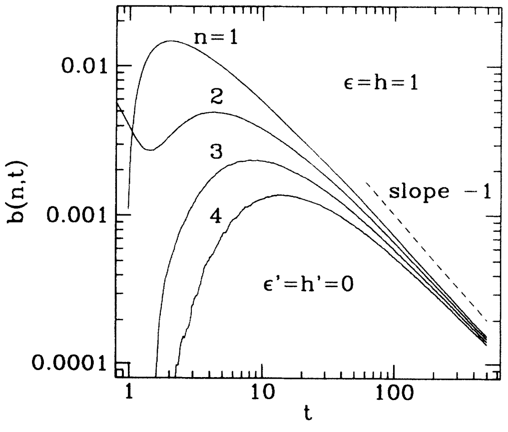

FIG. 6. Slow decay of connected correlation functions for nonsteady regimes. The initial state corresponds to an empty lattice of 10^5 sites; the averages were taken on 10^3 histories. For nearest-neighbor correlations ($n = 1$) the numerical data (solid lines) reproduce completely the theoretical results [Eqs. (79) and (80) in the text]. The asymptotic behavior of further neighbor correlations closely follows the results obtained in Sec. VI B 4 for the case $n = 1$.

VII. DISCUSSION

The preceding sections have used a wide ranging attack to obtain exact results for a generalized class of stochastic models particularly relevant to adsorption-desorption processes, surface reactions, and catalysis. The quantities obtained, namely, density, steady-state correlation functions, equal-time correlation functions, and current are those of principal interest.

It was found that the density typically relaxes exponentially, except in the conditions treated in Sec. V B and VI B 4. The steady-state autocorrelation function results usually show exponential decay with a variety of subdominant power-law factors. An exception with pure power-law decay is where $\epsilon = \epsilon', h = h'$ and one of ϵ or h vanishes. The equal-time correlation function for $h = h' = 0$ has for $\epsilon = \epsilon'$ a power-law form which depends on initial conditions; for nonzero diffusion its decay is typically exponential. The particle current is nonzero in the biased case and depends on the diffusion solely through a factor $h - h'$. All the main results have been confirmed through simulation.

Despite the considerable generalization accomplished, the treatment is still limited. All the calculations were carried out for the infinite system limit. Boundary conditions have been taken to be periodic. Sections II and III are the only ones which apply for any dimension d. No allowance has been made for defects (local rate modifications) or stronger disorder, or for deposition or evaporation of k-mers with $k \neq 2$ in addition to the dimer processes. The model also omits any thermal (activation) processes. Also the initial state that occurs in the non-steady-state results has been taken to be translationally invariant only. It would be interesting and important to attempt generalizations of all these. Finite size effects are certainly tractable, and the treatment of some non-translationally-invariant initial states seems feasible. The other generalizations are more difficult and in some cases prohibitively so. In particular the generalization to higher dimensions d for the equal-time correlation function of the system with $\epsilon = \epsilon', h = h' = 0$ might look likely using the XXZ mapping. But unfortunately this correlation function includes contributions from the two-spin-wave sector which is, so far, intractable beyond $d = 1$. Also the generalization of the Jordan-Wigner transformation to higher d, though it exists [17], is very difficult to apply. The effect of, e.g., open boundary conditions is interesting and not hopeless [18]: boundary conditions of course strongly affect the particle current and density profiles. A generalization to include defects has already been successful [19] for the case $\epsilon = \epsilon'$.

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