

Stationary Coverage of a Stochastic Adsorption–Desorption Process with Diffusional Relaxation

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We show that it is possible to derive the stationary coverage of an adsorption–desorption process of dimers with diffusional relaxation with a very simple ansatz for the stationary distribution of the process supplemented by a hypothesis of global balance. Our approach is compared to the exact result and we seek to understand its validity within an instance of the model.

KEY WORDS: Stochastic lattice gas; dimers; stationary state.

1. INTRODUCTION

The use of master equations is one of the most promising techniques in the study of nonequilibrium statistical systems, their success stemming both from their nice mathematical properties and from their phenomenological character, making them a modelling tool in a great variety of situations.

In order to set up the master equation for a model system, one is asked to give the transition rates between the different possible configurations of the system. Under rather weak conditions, namely that each configuration must be reachable from every other, one can assert that as time tends to infinity the probability distribution of configurations will tend, for finite systems, to a unique nonzero stationary distribution. In the case detailed balance holds among the rates, a condition that can be easily verified by perusal of the Kolmogoroff's criterion,⁽¹⁾ the matrix of the

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transition rates can be cast in the form DSD^{-1} with D diagonal and S symmetric,⁽²⁾ and the system's stationary distribution will be an equilibrium one such that we can assign to it an effective energy $H = \ln P_s$, simply related to the rates. When detailed balance does not hold, on the contrary, the determination of the stationary distribution becomes considerably a more involved task, its structure being in general almost completely unknown. Albeit such a distribution will exist, and a number of techniques have developed aiming at the evaluation, at least in an approximate fashion, of an energy function also in these cases; noteworthy among these is the correlation method.^(3, 4)

The purpose of this paper is to show how a very simple ansatz for the stationary distribution plus a hypothesis of global balance can be used to clarify some results for a reaction-diffusion process that was in vogue some time ago.⁽⁵⁻⁷⁾ The process consists of adsorption and desorption of dimers together with asymmetric diffusion of monomers on a one-dimensional lattice. The previously derived results for the process were obtained using a Schrödinger-like description of the master equation that renders the infinitesimal generator of the Markov semigroup a magnetic Hamiltonian aspect, thus allowing for techniques first developed in a magnetic context to be used in the stochastic context with equal profit.

The paper goes as follows. In Section 2 we derive the Schrödinger-like form of the master equation in the special case where only two states per site are present; we believe the derivation given there is clearer than the ones usually encountered, though it is not properly a novelty. We also define the model and state the results we are interested in. In Section 3 we make our contribution to the understanding of the stationary coverage of the model and in Section 4 we discuss our result in the light of previous exact results obtained for this quantity.

2. THE TIME EVOLUTION OPERATOR

Let us begin with the master equation. We consider a one-dimensional lattice $A \subseteq \mathbf{Z}$ of $|A| = L$ sites, and attach to each site $l \in A$ a random variable σ_l taking values on $\omega = \{-1, +1\}$, the state space of the whole lattice being given by $\Omega = \omega^A$. If $W(\sigma', \sigma)$ denotes the rate of transition between the configurations σ and σ' ($\sigma \rightarrow \sigma'$), $\sigma, \sigma' \in \Omega$, and $P(\sigma, t)$ is the probability of realization of a particular configuration σ at instant t , we write the master equation as

$$\frac{\partial P(\sigma, t)}{\partial t} = \sum_{\sigma' \in \Omega} [W(\sigma, \sigma') P(\sigma', t) - W(\sigma', \sigma) P(\sigma, t)] \quad (1)$$

Using the fact that in a one-dimensional lattice of two-state variables $|\Omega| = 2^L = |\{R \subseteq A\}|$ and also that the only possible channel of collision for a σ_l is $\sigma_l \rightarrow \sigma'_l = -\sigma_l$, we write the transition rates most generally as

$$W(\sigma, \sigma') = \sum_{R \subseteq A} W_R(\sigma') \delta(\sigma^R - \sigma'), \quad (2)$$

where by σ^R we mean the configuration which equals σ except for the sites in the region R , where $\sigma_r^R = -\sigma_r$, $r \in R$, and the delta is a product of Kronecker's deltas over the whole lattice. We then rewrite Eq. (1) as

$$\frac{\partial P(\sigma, t)}{\partial t} = \sum_{R \subseteq A} [W_R(\sigma^R) P(\sigma^R, t) - W_R(\sigma) P(\sigma, t)] \quad (3)$$

We now explicitly introduce linear vector spaces in the description of the structure of Eq. (3). To do this we turn $\omega = \{-1, +1\}$ into $\omega = \mathbf{C}^2$ and σ into $|\sigma\rangle = \otimes_{l \in A} |\sigma_l\rangle$, the state space now being given by $\Omega = \otimes_{l \in A} \omega$. Taking an orthonormal basis $\{|\sigma\rangle\}$ for Ω we write

$$|P(t)\rangle = \sum_{\sigma \in \Omega} P(\sigma, t) |\sigma\rangle \quad (4)$$

for the generating vector of the probability densities $P(\sigma, t) = \langle \sigma | P(t) \rangle$. In the space of the linear operators acting on Ω we define \hat{X}_R and \hat{W}_R by their actions

$$\hat{X}_R |\sigma\rangle = |\sigma^R\rangle \quad \text{and} \quad \hat{W}_R |\sigma\rangle = W_R(\sigma) |\sigma\rangle \quad (5)$$

Multiplying Eq. (3) by $|\sigma\rangle$ and summing over Ω , with the help of the above defined operators we eventually arrive at

$$\frac{\partial |P(t)\rangle}{\partial t} = -\hat{H} |P(t)\rangle \quad (6)$$

with

$$\hat{H} = \sum_{R \subseteq A} (\hat{1} - \hat{X}_R) \hat{W}_R \quad (7)$$

the infinitesimal generator of the Markov semigroup $\hat{T}(t) = \exp(-\hat{H}t)$. Equation (6) is in the desired Schrödinger-like form. If we use for the matrices of the \hat{X}_R and \hat{W}_R operators the basis of Pauli matrices with σ^z diagonal we readily see that

$$\hat{X}_R = \prod_{r \in R} \sigma_r^x \quad \text{and} \quad \hat{W}_R = W_R(\sigma^z) \quad (8)$$

where σ_r^α stands for $\sigma_r^\alpha = \hat{1} \otimes \dots \otimes \hat{1} \otimes \sigma^\alpha \otimes \hat{1} \otimes \dots \otimes \hat{1}$, the σ^α being in the r th position, $\alpha = x, y, z$.

The process we are interested in is one in which pairs of particles adsorb with rate ε and desorb with rate ε' from the lattice and which also admits diffusion of monomers to the right with rate h and to the left with rate h' .⁽⁵⁻⁷⁾ Identifying the presence of a particle in the site l with the eigenvalue $+1$ of σ_l^z we obtain from Eqs. (7) and (8) the two-body evolution operator

$$\hat{H}_{l,l+1} = (1 - \sigma_l^x \sigma_{l+1}^x) \frac{1}{4} [\varepsilon(1 - \sigma_l^z)(1 - \sigma_{l+1}^z) + \varepsilon'(1 + \sigma_l^z)(1 + \sigma_{l+1}^z) + h(1 + \sigma_l^z)(1 - \sigma_{l+1}^z) + h'(1 - \sigma_l^z)(1 + \sigma_{l+1}^z)] \quad (9)$$

notice that the collision operator $\hat{X}_{l,l+1} = \sigma_l^x \sigma_{l+1}^x$ is common to all the elementary processes of the model. The total evolution operator can be obtained summing the two-body operator over the sites of the lattice provided some boundary condition is given.

The operator in Eq. (9) is a very interesting and a very complicated one. From the magnetic point of view it is an *XXZ* Heisenberg ferromagnet with both *XY* and Dzyaloshinskii-Moriya (DM) in-plane interactions with pure imaginary couplings, plus an external field and, for open boundary conditions, a surface term. We can see, developing the products in (9), that the coupling in the *XY* term is associated to the difference of the adsorption and desorption rates, while that in the DM term is associated to the asymmetry in the diffusion. It is interesting to note that an asymmetric diffusion breaks the chiral symmetry that the system would have otherwise, and that this reflects in the DM term $(\vec{\sigma}_l \times \vec{\sigma}_{l+1}) \cdot \hat{e}_z$, that just does exactly the same thing.

With periodic boundary conditions the total operator resulting from Eq. (9) have been exactly solved for a number of choices of the rates.⁽⁵⁻⁷⁾ For example, for $\varepsilon = \varepsilon' = h = h'$ it reduces to the Ising model diagonal in the σ^x representation, and for $\varepsilon = \varepsilon' \neq h = h'$ it can be cast, after a rotation over the bipartite lattice, to a ferromagnetic *XXZ* Hamiltonian in one of its massive phases. In particular, for $\varepsilon + \varepsilon' = h + h'$ the evolution operator turns out to be quadratic in $\sigma^\pm = \frac{1}{2}(\sigma^x \pm i\sigma^y)$ and thus can be solved in terms of free fermions.^(5,6) It is to this instance of the model that we want to adress our observations.

3. THE STATIONARY COVERAGE

It is possible to interpret domain walls in the Glauber kinetic Ising model⁽⁸⁾ as particles in a reaction-diffusion scenario.⁽⁹⁾ Although in the original model domain walls diffuse symmetrically, this can be relaxed to

allow for biased diffusion without departing too much from the original structure of the equations of the model,⁽⁵⁾ though detailed balance and the connection with the equilibrium distribution of the Ising model do not hold in this case anymore. On the other hand the relationship between the Glauber model and free fermions have been established already a long time ago.⁽¹⁰⁾ All this led to the conclusion that whenever $\varepsilon + \varepsilon' = h + h'$ in the model described in the last section, one can associate to it a free fermion evolution operator that is also the evolution operator of an asymmetric version of the Glauber model.

The above mentioned relationships have made it possible to compute the time-dependent density profile of the model in the free fermion case, with the result that the stationary coverage is given by^(5,6)

$$\lim_{t \rightarrow \infty} \rho(t) = \rho_s = \frac{1}{1 + \sqrt{\varepsilon'/\varepsilon}} \tag{10}$$

We would like to rederive this result without recourse to the free fermion constraint.

Guided by the duality between domain walls and particles and by the product form of the equilibrium distribution of the Glauber model (since $\sigma_i^z \sigma_{i+1}^z \rightarrow \tau_i^z$ under the duality transformation) we ask whether we can derive any results by postulating a stationary distribution of the form

$$P_s(\sigma) = \prod_{l \in \mathcal{A}} P_s(\sigma_l) = \frac{1}{Z} \exp\left(J \sum_{l \in \mathcal{A}} \sigma_l\right) \tag{11}$$

where $Z = (2 \cosh J)^L$ is a normalizing constant. In doing this we were particularly inspired by the results in ref. 4. From the master equation (3) we see that $P_s(\sigma)$ will be stationary if

$$\sum_{R \subseteq \mathcal{A}} [W_R(\sigma^R) P_s(\sigma^R) - W_R(\sigma) P_s(\sigma)] = 0 \tag{12}$$

which is not the condition of detailed balance, since we are not requiring each term of the sum to vanish, but only the whole sum to vanish instead. Looking at the rate operator \hat{W}_R in Eq. (9) we see that we can write it as

$$\hat{W}_{l,l+1} = A + B\sigma_l^z + C\sigma_{l+1}^z + D\sigma_l^z \sigma_{l+1}^z \tag{13}$$

with $A = \frac{1}{4}(\varepsilon' + \varepsilon + h + h')$, $B = \frac{1}{4}(\varepsilon' - \varepsilon + h - h')$, $C = \frac{1}{4}(\varepsilon' - \varepsilon - h + h')$ and $D = \frac{1}{4}(\varepsilon' + \varepsilon - h - h')$; notice that under the free fermion condition $D = 0$, corresponding to the vanishing of the “many-body” term in Eq. (9). Since

we are dealing with a basis diagonal in the σ_i^z 's we will treat them in Eq. (13) as if they were c-numbers. From Eqs. (12) and (13) it follows that $P_s(\sigma)$ will be stationary if

$$\sum_{l \in \mathcal{A}} \{ W_{l,l+1}(\sigma^{l,l+1}) \exp[-2J(\sigma_l + \sigma_{l+1})] - W_{l,l+1}(\sigma) \} = 0 \quad (14)$$

and taking into account the translational invariance of the system we arrive at the following condition on the coupling constant J ,

$$\tanh 2J = -\frac{B+C}{A+D} = \frac{\varepsilon - \varepsilon'}{\varepsilon + \varepsilon'} \quad (15)$$

that is,

$$e^{-4J} = \frac{\varepsilon'}{\varepsilon},$$

and the stationary coverage per site reads

$$\rho_s = \frac{e^J}{e^J + e^{-J}} = \frac{1}{1 + \sqrt{\varepsilon'/\varepsilon}} \quad (16)$$

as in Eq. (10).

The above result is rather surprising. It states that in the stationary regime mean-field analysis, as expressed by (11), holds exact. It also tells us that despite the fact that when $h \neq h'$ a current of particles establishes in the substrate, in the stationary state the concentration of particles only depends upon the adsorption-desorption rates. Similar results have been obtained for the case $h = h' = 0$, but in this case the model shows microscopic reversibility and a "Boltzmann weight analysis" can be performed,⁽¹¹⁾ which in the case being is not an a priori valid procedure.

4. CONCLUSIONS

The expressions for the concentration of particles in the stationary state given by Eqs. (10) and (16), though identical, were obtained by very different techniques. Our result is mean-field-like but anyway we were able, with the aid of a hypothesis concerning global balance, to reproduce the exact result.

It is well known that both the symmetric and asymmetric simple exclusion processes have product form stationary distributions like that in

Eq. (11), i.e., they both have white noise as invariant measures, as is sometimes said. This however should not lessen one's surprise in having $P_s(\sigma)$ as in Eq. (11) for the process we are dealing with in this paper since it has, besides one particle exclusion, adsorption of dimers in which two adsorbed particles together prevent further adsorption, and when all four rates that define the model are non-null it is not possible by any amount of sublattice-mapping funambulism to turn the model into an instance of a simple exclusion process. Anyway, for $\varepsilon = \varepsilon' = 0$ our analysis breaks down, for in this case Eq. (15) becomes ill-defined. On the other hand, when $h = h' = 0$ but $\varepsilon \neq 0 \neq \varepsilon'$ the same result for ρ_s holds,^(5,11) and it thus appears that a finite amount of adsorption-desorption contrives ρ_s to be given by Eq. (16), which is indeed a curious result.

One possible explanation for this is that due to the similitude of the model with the Glauber model through a site-bond transformation one expects that in the particle scenario the expression given by Eq. (11) is a reasonable guess. It should be mentioned however that the exact duality demands $h = h'$, which in our approach is not necessary.

One can naively say that the stationary coverage does not depend on the asymmetry of diffusion due to the periodic boundary conditions: one then simply performs a Galilei transformation $l \rightarrow l + (h - h')t$ on the whole lattice and follows the time dependencies on the stationary state on the new reference frame, where the diffusion happens to be symmetrical and the exact duality with the Glauber model is recovered. This procedure, if plausible in some special circumstances, to date has been proved right only for a special class of initial distributions, the completely random ones, and in the free fermion point $\varepsilon + \varepsilon' = h + h'$.⁽⁷⁾

We would like to stress that we *guessed* the product form stationary distribution Eq. (11), and it happened that it contained coupling constants enough to allow for the derivation of Eq. (16), in the case only one coupling constant $J = J(\varepsilon, \varepsilon')$. It could equally well have happened that other couplings, say $K\sigma_l\sigma_{l+1}$ with $K = K(\varepsilon, \varepsilon', h, h')$, would have been necessary to derive useful results.

As a final remark we notice that the hypothesis of global balance and its connection with periodic boundary conditions can be further exploited, e.g., using open boundaries and adding the necessary currents of particles at the ends so to satisfy the same global balance equations, with $P_s(\sigma)$ possibly modified to account for the open boundaries.

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