Steady-state and transient properties of reaction-diffusion systems

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Abstract

In this paper we discuss different quantities that allow a characterization of steady-state and transient properties of nonequilibrium reaction-diffusion systems for which microscopic reversibility is broken. Using numerical exact techniques and numerical simulations we show that stationary probability currents allow to quantify the distance to equilibrium. When a system is forced out of a steady state, fluctuation ratios provide non-trivial insights into the microscopic dynamics of that system. © 2010 Published by Elsevier B.V. Open access under CC BY-NC-ND license.

1. Introduction

Understanding non-equilibrium systems remains one of the most important challenges in contemporary physics. Whereas progress has been made in specific cases (as for example in driven lattice gases), a general theoretical framework has yet to be developed.

In recent years different proposals have been made in order to characterize systems that are out of equilibrium. Some of these proposals aim at characterizing the steady-state properties of these systems [1, 2], others address aging phenomena in systems relaxing towards a steady state (be it an equilibrium or a non-equilibrium one) [3], and a third group of proposals focuses on the properties of systems that are forced out of stationarity [4, 5]. We discuss here different ways of characterizing lattice-gas systems with irreversible reactions. As this type of reactions leads to the breaking of microscopic reversibility, many of the quantities proposed for the investigation of out-of-equilibrium systems are ill-defined and can therefore not be used [6, 7].

We consider particles diffusing on a one-dimensional lattice with different reaction schemes, see Table 1. In every model we have a creation process, where a new particle is created with rate $h$, and an annihilation process, where at least one particle is destroyed with rate $\lambda$. These creation and annihilation processes are chosen in such a way that the models present different degrees of microscopic reversibility. Thus in model 1 all reactions are reversible, and it is easy to see that this model is in chemical equilibrium for fixed values of the reaction and diffusion rates. In model 2 some reactions are irreversible. For example, a new particle can be created in the middle of two empty sites, $000 \rightarrow 0A0$, with rate $h$, but it is not possible to go back immediately to three empty sites as the newly created particle needs a neighbor for the annihilation process to take place.
Finally, all reactions are irreversible in model 3. These various levels of microscopic reversibility allow us to study systematically the out-of-equilibrium properties of reaction-diffusion systems.

\[
\begin{array}{ccc}
\text{model 1} & \text{model 2} & \text{model 3} \\
A + A \rightarrow 0 + A & A + A \rightarrow 0 + A & A + A \rightarrow 0 + 0 \\
A + 0 \stackrel{h}{\rightarrow} A + A & 0 \rightarrow A & 0 \rightarrow A \\
\end{array}
\]

Table 1: The different reaction schemes discussed in this work.

2. Steady-state properties

For all three models the probability \(P(C_i, t)\) to find the system in configuration \(C_i\) at time \(t\) is described by the discrete-time master equation

\[
P(C_i, t + 1) - P(C_i, t) = \sum_j \left[ \omega(C_j \rightarrow C_i) P(C_j, t) - \omega(C_i \rightarrow C_j) P(C_i, t) \right],
\]

where \(\omega(C_i \rightarrow C_j)\) is the transition probability from configuration \(C_i\) to configuration \(C_j\). Microscopic irreversibility means that some of the transition probabilities \(\omega(C_i \rightarrow C_j) = 0\) even though \(\omega(C_j \rightarrow C_i) > 0\). It has been proposed [1] that systems described by equation (1) should be characterized by both the stationary probability distribution \(P_s(C_i)\) and the stationary probability currents between two configurations \(C_i\) and \(C_j\):

\[
K'(C_i, C_j) = \omega(C_j \rightarrow C_i) P_s(C_j) - \omega(C_i \rightarrow C_j) P_s(C_i).
\]

In the following we discuss results obtained for small systems using numerical exact techniques [6, 7]. Larger systems, which can be studied through standard Monte Carlo simulations, yield results compatible with the data presented here.

In Figures 1 and 2 we discuss the stationary probabilities and the stationary probability currents for our three systems. In order to compute the stationary probabilities we set up the transition probability matrix whose elements are the transition rates between different configurations. For a system of length \(L\) the transition probability matrix is a \(2^L \times 2^L\) matrix. The stationary probabilities \(P_s(C_i)\) are then the elements of the null eigenvector of the matrix which results when subtracting off the identity matrix from the transition probability matrix. Comparing the stationary probabilities for models 1 and 3, see Figure 1, quantitative differences are observed. However, it is not possible to distinguish between the equilibrium model 1 and the nonequilibrium model 3 by only looking at these stationary probabilities.

In fact, the stationary probability currents are much more revealing, as shown in Figure 2 where we plot for the three models the global quantity \(K = \sum_{i,j \neq i} |K'(C_i, C_j)|\) as a function of the creation rate \(h\) for fixed \(\lambda\) and \(D\). As expected \(K\) is zero for our equilibrium system 1. The nonequilibrium models 2 and 3, however, are characterized by nonvanishing stationary probability currents. The value of \(K\) decreases in model 2 for larger \(h\) but increases for model 3. This is understood by remarking that for larger values of \(h\) configurations with a large number of particles have an increased stationary probability, see Figure 1. As a result, free sites will have with high probability occupied neighboring sites, and the creation process \(0 \rightarrow A\) effectively
equals the process $A \rightarrow 2A$. This is, however, exactly the reversed reaction to the annihilation process of model 2, which explains why for large $h$ the behavior of model 2 approaches that of an equilibrium system. For model 3 all reactions remain irreversible and $K$ keeps on growing.

3. Transient behavior

Whereas in the previous section we focused on the steady-state properties, we shall discuss in the following the transient properties of reaction-diffusion systems when forcing them out of a stationary state. We are realizing this through a protocol in which we change one of the reaction rates $r$ from an initial value $r_0$ to a final value $r_M$ in $M$ equidistant steps of length $\Delta r$, yielding for the reaction rate the values $r_i = r_0 + i\Delta r$ with $i = 0, \ldots, M$. We thereby assume that at every step only one reaction or diffusion process takes place.

As we are dealing with systems in which microscopic reversibility is broken, we have to be careful with the choice of our observable. Indeed, many of the quantities studied in the context of fluctuation theorems assume that if a reaction rate between two configurations is non-zero,
then also the rate for the inverse process is different from zero [8]. Obviously, this assumption is not fulfilled for our models 2 and 3.

Hatano and Sasa [9] proposed a quantity that does not assume microscopic reversibility. Adapting this quantity for systems driven out of stationarity [10], we have [6, 7]

$$\phi = \sum_{i=0}^{M-1} \ln \left[ \frac{P_s(C_i, r_i)}{P_s(C_i, r_{i+1})} \right]$$

where $P_s(C_i, r_i)$ is the probability to find the configuration $C_i$ in the stationary state corresponding to the value $r_i$ of the reaction rate $r$. The quantity $\phi$ is called the driving entropy production [10].

Figure 3 shows the probability distributions of $\phi$ for our three models. For both forward and reversed processes these probability distributions are characterized by prominent peaks. Interestingly, an increase of the diffusion constant amplifies these peaks without changing the overall shape of the probability distributions. This indicates that these peaks are related to trajectories in configuration space that are dominated by diffusion steps and not by reactions.

One should note that these peaks do not have their origin in the noisiness of some numerical data, but are real as we are using a numerically exact method. Our approach also allows us to circumvent any issues that might appear due to an insufficient sampling of rare events. This is of importance when discussing the ratios of the forward and reversed probability distributions.

Figure 3: Probability distributions for $\phi$ when the creation rate $h$ is changed in $M=6$ steps from 0.2 to 1.4 ($P_f(\phi)$, black curve) or from 1.4 to 0.2 ($P_r(-\phi)$, green (gray) curve), with $L = 8$, $D = 5$ and $\lambda = 1$.

Even though in systems obeying detailed balance $\phi$ is related to the work done on the system, one does not expect that this quantity fulfills an exponential detailed fluctuation relation [5] in systems with nonequilibrium stationary states. We show in Figure 4 ratios of the probability distributions of $\phi$ in forward and reversed processes. For model 2 the deviations from the exponential are random and no pronounced dependence on system parameters is observed. For model 3, however, systematic deviations in the form of oscillations are encountered.

In order to understand the origin of these oscillations we need to go back to the different reaction schemes summarized in Table 1. The configuration space of a reaction-diffusion system can be thought to be composed of smaller units formed by the configurations with a common number $N$ of particles. A diffusion step conserves the number of particles, thereby connecting two configurations in the same unit. A passage from one unit to another always involves a change of particle number and is therefore exclusively due to a reaction process. Keeping this in mind, a fundamental difference emerges between models 1 and 2 on the one hand and model
Figure 4: Fluctuation ratios for the observable $\phi$ for model 2 and model 3 and different values of the diffusion constant $D$. Whereas in model 2 only random deviations from a simple exponential behavior are observed, systematic deviations show up for model 3, see upper panels. In the lower panels we subtract $\phi$ from the logarithm of the fluctuation ratio. The parameters used in this calculation are $L = 8$, $h_0 = 0.2$, $\Delta h = 1.2$, and $\delta = 1$, and the driving length is $M = 6$.

3 on the other hand. In the former systems every reaction changes the particle number by 1, $\Delta N = \pm 1$. In the latter systems, however, also larger changes in the particle number happen in the annihilation process, with $\Delta N = -2$. It is this difference in the number of particles created in a creation process or destroyed in an annihilation event that yields contributions to the probability distributions which are not compensated in the fluctuation ratio [6, 7].

We expect these results to be generic, yielding similar signatures also in other system classes with a configuration space topology that is similar to that of the reaction-diffusion systems (i.e., composed by groups of configurations that are only connected in a very specific way) and with a similar asymmetry in the configuration space trajectories.

Supported by the U.S. National Science Foundation through Grant No. DMR-0904999.

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