Spatial correlation of concentration fluctuations in reaction diffusion problems by the Gillespie algorithm

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During the last decades the spectrum of thermal fluctuations in non-equilibrium systems has been widely studied. It has been shown that static correlations have generically long range behavior, while the fluctuations around equilibrium states are, except in the neighborhood of critical points, short ranged. These investigations may be helpful to elucidate whether or not there exist thermodynamic potentials out of equilibrium, and could exclude the local potentials.

Among the non-equilibrium states that have been studied theoretically, there are examples of reaction-diffusion systems in which the inverse chemical reaction and the direct chemical reaction occur through different paths, avoiding chemical equilibrium. It is hard to devise an experimental set up to verify the theoretical conclusions in this case, because it is difficult to find a two-component system whose kinetics is as simple as the ones theoretically studied. A numerical simulation could be a better way to confirm the theory for this kind of problems. More over, there are so far very few simulations that focus on non-equilibrium fluctuations. This is why a simulation of equilibrium and non-equilibrium reaction-diffusion problem is of current interest.

The Gillespie algorithm[1] is a Montecarlo method that simulates efficiently a system of chemical reactions through the chemical master equation. Although it was developed in 1976, the interest in this algorithm has grown during the last years, particularly because of its proven utility in Biophysical problems. The Gillespie algorithm was originally conceived to describe a large network of coupled chemical reactions, but it can be applied to diffusion processes as well, by assuming that the diffusion of one particle from one domain of the system to other can be handled as a chemical reaction with a certain probability[2].

We have developed a computer code to simulate, via the Gillespie algorithm, isothermal reaction-diffusion problems in one dimension. We have performed extensive simulations to numerically study the statistical correlations of the concentration fluctuations at different spatial spots, in order to verify that such correlations are shot-ranged if the chemical reactions are in equilibrium and long-ranged if they are not in equilibrium. We studied the system with an equilibrium chemical reaction (a simple association-dissociation)

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B, \tag{1}$$

while, as an example of a non-equilibrium reaction, we studied the nonzero stationary state of the WOH model[3]:

$$A \xrightarrow{k_1} B,$$
$$A + B \xrightarrow{k_2} 2A. \tag{2}$$

As an example of our results, we show in Fig. 1 the real-space correlation functions of concentration fluctuations in reaction-diffusion problems corresponding to the chemical kinetics of Eq. (1) (equilibrium, top panel) and of Eq. (2) (nonequilibrium, bottom panel). Short-ranged behavior in the first case and long-ranged in the second case, as predicted by the theory, are obvious. Diffusion coefficients are the same in both cases.
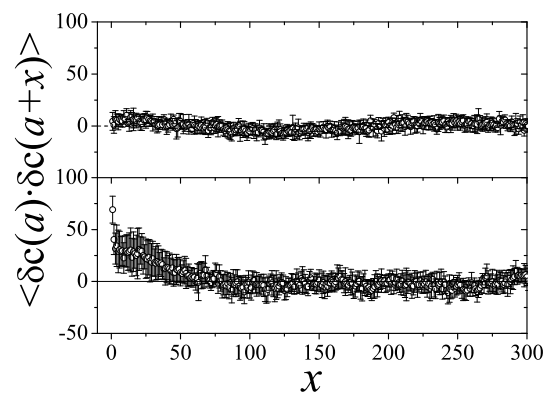

FIG. 1. Real-space correlation function of concentration fluctuations in equilibrium (top panel) and outside of equilibrium (bottom panel).

In addition, we have studied the validity of the van Kampen approach in an homogeneous reacting system, and estimated the number of particles N at which the probability distribution of the fluctuations can be assumed as gaussian. We have applied the Gillespie algorithm to a pure diffusion problem as well, and checked its validity by verifying that the variance of the fluctuations are, as expected, equal to the square root of the mean number of particles at every spot.

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