Fast nonequilibrium Monte Carlo simulations

Heinz–Peter Breuer, Wolfgang Huber and Francesco Petruccione

Albert-Ludwigs-Universität, Fakultät für Physik,
Hermann-Herder Straße 3, D–79104 Freiburg im Breisgau, Federal Republic of Germany

Abstract

Monte Carlo simulation algorithms in many cases spend most of their time on selecting the next transition. We investigate the performance of different selection schemes for systems in which a transition leads to a change in many transition rates, e. g. large chemical reaction systems. A fast new method is based on the construction of a multivariate master equation which assigns equal rates to all transitions but lets them have appropriately varying transition step widths.

Monte Carlo simulations are a powerful tool for the study of non–equilibrium dynamics. The selection of the next event is often the time–critical part of the algorithms. Transition selection methods proposed in the literature [1-6] are optimized for systems in which each state transition changes only a few transition rates. This article presents a way to handle systems which do not fall into this class in substantially less computer time.

Let the system's state be described by a set of variables $N = (N_1, \ldots, N_J)$. For instance, when dealing with chemical or reaction–diffusion processes, N_i is the number of a species in a certain finite volume element, i labelling both the different species and the different volume elements. The system's stochastic dynamics is most conveniently described in terms of a master equation for the probability distribution $P_N(t)$ on the state space [7]. It can be written in the form

$$\frac{d}{dt} P_N(t) = \sum_{N'} \left(W_{N,N'} P_{N'}(t) - W_{N',N} P_N(t) \right) \ . \tag{1}$$

Monte Carlo algorithms generate a sample of independent realizations of the stochastic process, from which all quantities of interest are estimated [1, 2]. The main loop of such an algorithm usually looks as follows:

1. Suppose the system is in state N at time t. The random waiting time τ until the next transition occurs is drawn from an exponential distribution with mean $\langle \tau \rangle = (\sum_{N'} W_{N',N})^{-1}$. Set $t := t + \tau$.

2. Choose a random transition. The transition $N \to N'$ has the probability $P[N \to N'] = W_{N',N} / \sum_{N'} W_{N',N}$.

3. Perform the corresponding changes in all relevant variables, and go to 1.

Various methods have been proposed for the implementation of step 2. In the rather simple *linear search* method [1], all possible transitions are arranged in a single linear list. A random

transition is selected by comparing the cumulative probability distibution with a uniformly distributed random number. This algorithm is reported to be sensitive to imperfections in the random number generator [3]. For large search spaces, it is expected to be slow, however a well-chosen arrangement of the transitions in the list may sometimes do a good job. In the *rejection method* [2], the transitions (or alternatively, small groups of transitions) are paired with null–transitions, such that the total rates of the pairs are all the same. The *null–process method* [3] is a slight modification. Such methods are best suited when the transition rates are all of the same order of magnitude, and are, in general, inefficient when the rates vary in a wide range. In order to achieve a more or less homogeneous distribution of rates, the transitions can be arranged in *logarithmic classes* [4]. Efficient searching in the space of transitions is performed by *multilevel search* or *binary tree methods*, where the set of possible transitions is arranged in a tree. These methods are generalizations of the binning method [6, 5]. It is clear that sophisticated search algorithms like the multilevel search can speed up step 2 considerably compared to simpler methods. However, in some systems the performance gain in step 2 can be outweighted by time-consuming bookkeeping in step 3. In order to qualify this statement, it is helpful to classify at least two types of systems:

I. After a transition $N \to N'$, only a small number of transition rates is changed, i. e. $W_{M,N'} = W_{M,N}$ for almost all M. This is typically the case for reaction–diffusion systems with a small number of species and a large number of spatial cells. Clearly, a reaction within one cell does not affect the rates in the others, and a diffusion step only affects the rates of the cells involved.

II. A transition changes a large number of transition rates. This is typical for large chemical reactions systems, where the number of species is large and each molecule can react with all or many of the other molecules. We shall present as an example an aggregation or polymerization reaction. In such cases the updating of a complicated data structure like a tree can consume much CPU time, and the bookkeeping time becomes comparable or even larger than the search time.

In order to achieve fast Monte Carlo simulations also for systems of type II, it can be advantageous to use instead of the master equation (1) an alternate one. The basic idea is to circumvent time–consuming selection or bookkeeping procedures by by assigning *equal rates* to all possible transitions, but giving them appropriately varying transition step widths. The state variables $x = (x_1, \ldots, x_J)$ of the alternate stochastic process will therefore in general be real–valued. If one starts from a master equation in the form (1), an alternate process can, for example, be constructed by defining, for each transition $W_{N',N} \neq 0$ in the original process, a corresponding transition

$$
\begin{aligned}
x &\mapsto x' = x + \alpha \Delta t \, (N - N') \, W_{N',N} \\
W_{x',x} &= \frac{1}{\alpha \Delta t} \; .
\end{aligned}
\tag{2}
$$

α is a dimensionless parameter which can be interpreted as the inverse system size, and Δt a characteristic time constant. Since $W_{x',x}$ is independent of x and x', the selection of the next transition in step 2 of the simulation algorithm simply amounts to drawing a uniformly distributed random number, and no auxiliary list or tree data structures need to be updated in step 3. Since the waiting time distribution does not change with time, the central limit theorem even allows to leave away step 1 and to calculate the elapsed time simply from the number of loop cycles.

Consider as example an irreversible polymerization or coagulation reaction. Here, each

chemical master equation, $\Omega = 250000$

new method, $\alpha = 0.01$

r.m.s. error

number of realizations
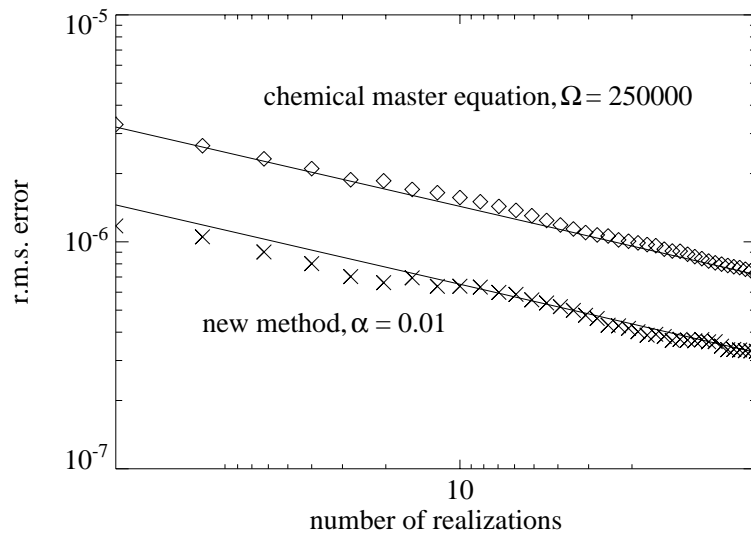
CPU time	
New method	1
Linear search	65
Rejection method	325
2-level tree	94
6-level tree	225
10-level tree	394

chain length or particle size i constitutes a separate species, and reactions of the type

$$X_i + X_j \xrightarrow{k_{ij}} X_{i+j} \tag{3}$$

are possible for each pair (i, j). The quantities k_{ij} denote the reaction rates. We have performed simulations of the chemical master equation that corresponds to this reaction, using the following selection schemes: linear search, rejection method and multi–level tree search method with 2, 4 and 10 levels. Particle sizes i from 1 to 1100 were represented in the simulations. The chemical master equation depends on a system size parameter Ω, which is equal to the total number of monomers [7, 8].

In the new master equation, instead of integer occupation numbers N_i, the stochastic variables x_i are real–valued and represent the concentrations of particles of size i. The transitions are labelled by the index pair (i, j), all have the same rate and are given by

$$
\begin{aligned}
x_i &\mapsto x_i - \frac{1}{2}\alpha\Delta t\, k_{ij} x_i x_j \\
x_j &\mapsto x_j - \frac{1}{2}\alpha\Delta t\, k_{ij} x_i x_j \\
x_{i+j} &\mapsto x_{i+j} + \frac{1}{2}\alpha\Delta t\, k_{ij} x_i x_j \quad .
\end{aligned}
\tag{4}
$$

This new master equation is obtained from the chemical master equation by using equation (2).

The figure shows the r.m.s. error obtained by comparing the particle concentrations estimated from the stochastic simulations to those obtained from an analytical solution. The plot confirms that simulations based on the chemical master equation and simulations based on equations (4) both yield the same correct results for the expectation values. The r.m.s. error is approximately proportional to the inverse square root of the number of realizations. Comparing such plots for different system size parameters Ω resp. α, but using the same simulation method, one finds that the *CPU time* needed to achieve a given maximal r.m.s. error does not depend on those parameters and is characteristic for each method. Hence, this quantity is a useful measure for the computational efficiency of the different methods. The relative CPU time consumptions, measured in units of the time consumption of the fastest method, that we have obtained in this way are listed in the table [9].

The bad performance of the tree methods indicates that the example is in fact, following the classification from above, a representant of case II systems. The result of the rejection method indicates that the transition rates of the chemical master equation vary in a wide range. The comparatively good performance of the linear search is likewise explained by the fact that the large transition rates are, for the given initial conditions and time range, those with small i and j, and the search starts at the right end.

The new method is not slowed down by time–consuming selection and bookkeeping procedures, and for the given problem, proves to be about 65 times faster than the fastest simulation based on the discrete master equation. Similar results can generally be expected for systems of case II.

The master equation defined by (2) describes, of course, a different stochastic process than the original one (1). Therefore, higher–order moments will in general be different. However, in the macroscopic limit the two master equations lead to the same equations of motion for the first moments, i.e. for the expectation values. This was exemplified in the simulation presented above. To prove this statement, van Kampen's system size expansion can be employed [7, 9–11]. With the help of this expansion it is possible to derive macroscopic equations for the expectation values $\langle N_i \rangle$ and $\langle x_i \rangle$, as well as for higher moments, from mesoscopic master equations. These macroscopic equations are valid in the limit of large system size.

Furthermore, given any set of differential equations, it is now straightforward to construct a stochastic process with equal transition rates like in equation (2) and which has these equations as its macroscopic equations.

References

[1] D. T. Gillespie, J. Comput. Phys. **22**, 403 (1976).

[2] K. Binder, *Monte Carlo Methods in Statistical Physics*, (Springer–Verlag, Berlin, 1979).

[3] P. Hanusse and A. Blanché, J. Chem. Phys. **74**, 6148 (1981).

[4] T. Fricke and J. Schnakenberg, Z. Phys. B **83**, 277 (1991).

[5] P. A. Maksym, Semicond. Sci. Technol. **3** 594 (1988).

[6] J. L. Blue, I. Beichl and F. Sullivan, Phys. Rev. E **51**, R867 (1995).

[7] N. G. van Kampen, *Stochastic processes in physics and chemistry*, (North–Holland, Amsterdam, 2nd ed., 1992).

[8] H. P. Breuer, J. Honerkamp and F. Petruccione, Chem. Phys. Lett. **190**, 199 (1992).

[9] H. P. Breuer, W. Huber and F. Petruccione, Phys. Rev. E **53**, 4234 (1996).

[10] H. P. Breuer and F. Petruccione, Phys. Lett. A **185**, 385 (1994).

[11] H. P. Breuer and F. Petruccione, Phys. Rev. E **50**, 2795 (1994).