



ORIGINAL ARTICLE

Implementation of Net-Event Monte Carlo algorithm in chemical kinetics simulation software of complex isothermal reacting systems

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Abstract Many stochastic methods are available for kinetic simulation of a spatially homogeneous chemical or biochemical reacting system. These methods become time costing for very complex systems with huge mechanism as in combustion reactions or even with moderate mechanism with stiffness. In this work, a new algorithm based on Net-Event Kinetic Monte Carlo (NEKMC) method is implemented to improve the Kinetic Monte Carlo (KMC) method of simulation by reducing the calculation time. A set of N reversible reactions, in a given mechanism, is considered as $2N$ elementary reactions in the KMC method, but in the NEKMC method just N reactions are considered. For each reversible reaction, the net-probability can be calculated by using the absolute value of the difference between the rates of the forward and the reverse reaction. By doing this, the number of events is divided by two and should reduce consequently the calculation time. This new method (NEKMC) is described and tested on complex systems and speediness of the program is compared for this method to the old one (KMC).

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1. Introduction

The simulation of chemical reactions plays an important role in various fields, such as combustion, air pollution, and chemical industry or in chemical education. This simulation can be achieved either by deterministic or stochastic methods. In deterministic methods we have to solve the differential equations system constituted of total rate equations of all species, that is to say, to find a way to express the variation of concentration versus time for each species. In very rare cases where the reaction mechanisms are very simple, it is possible to find exact analytical solutions for the system of differential equations. In the remaining cases we must accept approximate solutions. These approximate solutions are generally obtained by

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numerical integration methods such as Euler (direct and indirect), Runge-Kutta (second or fourth order), Gear methods and others (Bamford and Tipper, 1983; Wilcomb and Bernstein, 1977; Noskov and Smooke, 2005; Shiang, 2009). The stochastic approach is quite different (Gillespie, 2007, 1977; Carstensen and Dean, 2007; Henriksen and Hansen, 2008). We have to calculate for each step (elementary reaction) the probability defined as the ratio of its rate to the sum of all steps rates. A random number is generated and compared to the probabilities in order to choose an elementary reaction. A chosen elementary reaction is executed by decreasing the number of molecules of reactants and increasing the number of molecules of products according to their stoichiometric coefficients. A new random number is generated and the same process is repeated until the end of reaction. Here also, there are several types of algorithms of stochastic simulation; known as “Kinetic Monte Carlo” (KMC) (Gibson and Bruck, 2000; Gillespie, 2001; Haseltine and Rawlings, 2002). These algorithms are intended to minimize the computation time, which tends to dramatically increase with increasing the number of mechanism steps.

The principal objective of our current work is also the minimization of the computation time. An important improvement to our previously described software (Tighezza et al., 2005) is achieved. Our software was based on KMC algorithm, and allows simulation of any reaction mechanism with no limit on the number of steps of this mechanism or the number of species. This improvement is achieved by implementing “Net Event Kinetic Monte Carlo” (NEKMC) algorithm, suggested by Snyder et al. (2005), in order to reduce the computation time. In this algorithm, any reversible step in the mechanism is reduced to a single event, unlike the KMC method which considers it as two separate events. If all steps, in a given mechanism, are reversible then it would reduce the number of events by half and the computation time should decrease significantly. This method offers a major advantage for reactions with “stiffness” conditions.

2. The model

Let us consider a mechanism constituted by X steps, each step is a reversible reaction (then with $2X$ elementary reactions), with Y species. The molecularity of elementary reactions is generally less or equal to three, then we can represent the i th step by:

$$\sum_{j=1}^3 (v_{ij}R_{ij} - w_{ij}P_{ij}) = 0 \quad (1)$$

and its rate by:

$$V_i = k_i \prod_{j=1}^3 [R_{ij}]^{v_{ij}} - k_{-i} \prod_{j=1}^3 [P_{ij}]^{w_{ij}} \quad (2)$$

where k_i represent the rate constant of the forward reaction and k_{-i} that of the reverse one. $[R_{ij}]$ (or $[P_{ij}]$) is the concentration of the j th reactant (or product) in this step and v_{ij} (or w_{ij}) the stoichiometric coefficient for the reactant or product, respectively. This rate could be either positive or negative and this sign will fix the choice of the forward or reverse reaction when this i th step is chosen.

At some time t , the probability P_i for the i th step to be chosen is:

$$P_i = \frac{|V_i|}{\sum_{i=1}^X |V_i|} \quad (3)$$

The summation of all these probabilities gives one, then we distribute them on the interval 0–1 by defining a new variable $Prob(i)$ like this:

$$Prob(1) = P_1 \text{ and } Prob(i) = Prob(i-1) + P_i \quad (4)$$

and we get evidently $Prob(X) = 1$.

We generate a random number Rnd in the interval 0–1 and we compare it to the probabilities previously calculated. If this random number is situated between the probabilities $Prob(i-1)$ and $Prob(i)$,

$$Prob(i-1) < Rnd \leq Prob(i) \quad (5)$$

then the i th step (reversible reaction) is chosen. According to the rate V_i sign, we execute the forward reaction if $V_i > 0$; or the reverse reaction if $V_i < 0$. The number of molecules of the reactants is reduced by v_{ij} and the number of molecules of the products is increased by w_{ij} in the first case and inversely for the second case. The reaction time is adjusted according to the following formula:

$$\Delta t = \frac{1}{\sum_{i=1}^X |V_i|} \quad (6)$$

Once these adjustments finished, we recalculate the reaction rates and probabilities and then start a new loop similar to the previous one, until a certain time t_{fin} (previously defined by the user) is reached. A simplified flow chart of this model is presented in Fig. 1.

3. Validity tests

To verify the validity of this model the reaction (M1) (without reversible steps) and (M2) (with three reversible steps) were simulated.



The reaction (M1) has a well-known analytical solution and the test is to compare the values calculated by our model to the values obtained from analytical solution. For the cyclic reaction (M2), we compared the simulated values of our model with the values obtained by using the Euler method.

3.1. Results obtained for the reaction (M1) $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

This reaction was simulated in the following conditions: $k_1 = 0.2 \text{ s}^{-1}$, $k_2 = 0.1 \text{ s}^{-1}$, $[A]_0 = 1$ (arbitrary unit), $[B]_0 = [C]_0 = 0$. Stochastic methods accuracy depends on the number of molecules in the initial sample (N_0). We realized the simulation with three different values for this parameter; $N_0 = 10^4$, 10^5 , and 10^6 molecules. The accuracy is even better

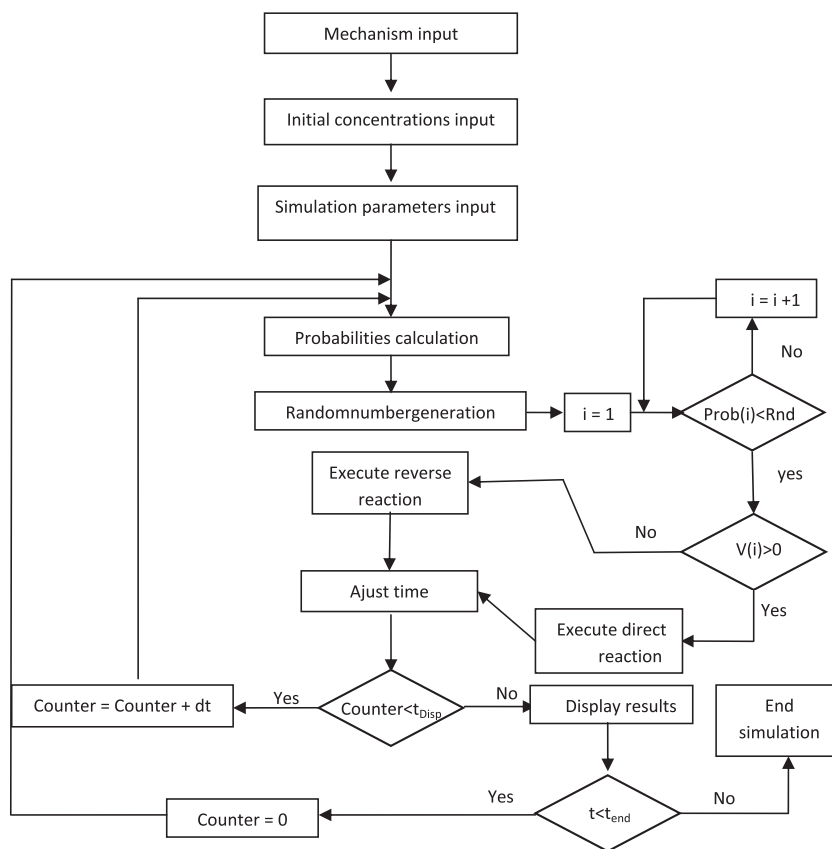


Figure 1 Flow chart of the NEKMC algorithm.

when the value of N_0 is higher. The simulation results with the first value ($N_0 = 10^4$), which is the least precise, are drawn on the same graph (Fig. 2) with the values calculated from analytical solutions given by the equations:

$$[A] = [A]_0 \exp(-k_1 t) \quad (7)$$

$$[B] = [A]_0 [\exp(-k_1 t) - \exp(-k_2 t)] / (k_2 - k_1) \quad (8)$$

$$[C] = [A]_0 - ([A] + [B]) \quad (9)$$

We can see in Fig. 2 that the two curves are almost identical. An average percentage of the difference between the simulated concentration of A (with our model: $[A]_{sim}$) and the calculated one (from analytical solutions: $[A]_{calc}$) is calculated as follows:

$$\Delta[A]\% = \frac{100|[A]_{calc} - [A]_{sim}|}{[A]_{calc}} \quad (10)$$

This relationship is applied to 40 points covering reaction time up to 95% consumption of reactant A. Differences being positive and negative, the absolute value is taken in the calculation of the average. Table 1 summarizes the values of this average for different values of the N_0 parameter and we can see that it decreases with increasing N_0 . Fig. 3 shows the distribution of calculated differences over the time range used. In general, it is less than 2.5% and decreases with increasing N_0 . We note also that it tends to increase over time.

3.2. Results obtained for the cyclic reaction (M2)

This reaction is simulated by using the Euler method in Excel spreadsheet with an integration step of 10^{-5} s which is very

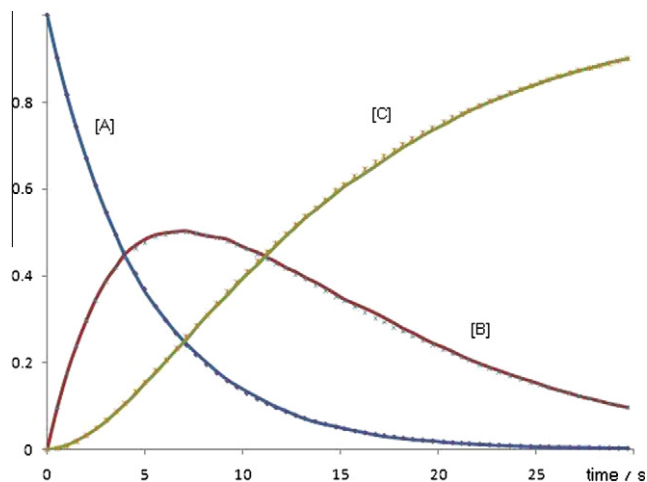


Figure 2 Comparison of simulated curves (solid lines) with curves obtained from analytical solutions (dotted lines) for the reaction (M1).

Table 1 Variation of the average value of the deviation according to N_0 values.

N_0 /molecules	10^4	10^5	10^6
$\Delta[A]\%$	0.80	0.54	0.31

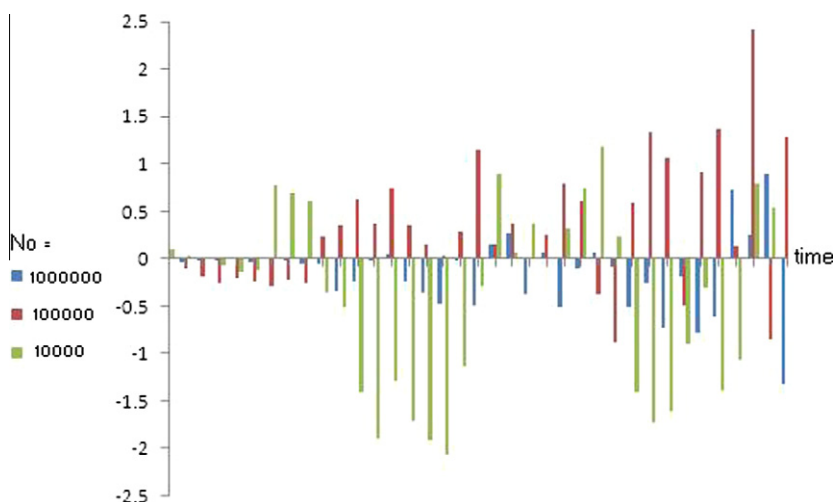


Figure 3 Evolution of the deviation (in%) versus time for three values of N_0 .

acceptable for such simple mechanism. The rate constants used are: $k_1 = 0.1 \text{ s}^{-1}$, $k_2 = 0.2 \text{ s}^{-1}$, $k_3 = 0.3 \text{ s}^{-1}$, $k_4 = 0.4 \text{ s}^{-1}$, $k_5 = 0.5 \text{ s}^{-1}$ which are chosen arbitrary, but the last constant k_6 is calculated from the following relation to satisfy the global equilibrium.

$$k_6 = \frac{k_2 k_3 k_5}{k_1 k_4} = 0.75 \text{ s}^{-1} \quad (11)$$

The initial concentration used are $[A]_0 = 1$ (arbitrary unit), $[B]_0 = [C]_0 = 0$.

Two values of N_0 , namely 10^5 and 10^6 , are used for the simulation of this reaction in our software, and the results are compared to those obtained with the Euler method as illustrated in Table 2. The results obtained with the NEKMC method are very similar with those obtained with the Euler method.

4. Software rapidity tests

As mentioned in our abstract, the main goal of our work is to reduce the computation time of the simulation. A great improvement is achieved with the implementation of NEKMC

algorithm in our software. For the purpose of illustration of this improvement, we have simulated the reactions (M1) and (M2) mentioned above and a third reaction Eq. (M3) with stiffness situation (fast equilibrium followed by a slow step: $k_1 = 10 \text{ s}^{-1}$, $k_{-1} = 9 \text{ s}^{-1}$ and $k_2 = 0.1 \text{ s}^{-1}$):



4.1. Rapidity test with reaction (M1) and (M2) (without stiffness situation)

The reactions (M1) and (M2) are simulated in similar conditions with our old software (with KMC algorithm) and a new one (with NEKMC algorithm) for a reaction time of 10 s. The computation time obtained for the two algorithms with the values $N_0 = 10^5$ and 10^6 is resumed in Table 3. As expected for the reaction (M1), without reversible steps, the computation time is the same for $N_0 = 10^5$, but KMC is better than NEKMC for $N_0 = 10^6$. The NEKMC method is devoted to reactions with reversible steps and contains many additional instructions for the reversibility purpose. Evidently, if the reaction does not include reversible steps, these additional instruc-

Table 2 Comparison of the NEKMC results for the reaction (M2) with those obtained with the Euler method.

Time/s	A/arbitrary unit			B/arbitrary unit			C/arbitrary unit		
	Euler	NEKMC		Euler	NEKMC		Euler	NEKMC	
		$N_0 = 10^5$	$N_0 = 10^6$		$N_0 = 10^5$	$N_0 = 10^6$		$N_0 = 10^5$	$N_0 = 10^6$
0.20	0.8938	0.8938	0.8937	0.0204	0.0203	0.0203	0.0858	0.0859	0.0860
0.40	0.8107	0.8109	0.8108	0.0409	0.0406	0.0409	0.1484	0.1485	0.1484
0.60	0.7453	0.7459	0.7453	0.0607	0.0608	0.0604	0.1940	0.1933	0.1943
0.80	0.6936	0.6939	0.6936	0.0793	0.0795	0.0789	0.2271	0.2266	0.2275
1.00	0.6524	0.6527	0.6525	0.0966	0.0966	0.0962	0.2510	0.2507	0.2513
1.20	0.6194	0.6198	0.6194	0.1123	0.1126	0.1119	0.2683	0.2676	0.2687
1.40	0.5927	0.5930	0.5927	0.1266	0.1269	0.1261	0.2807	0.2801	0.2811
1.60	0.5710	0.5715	0.5711	0.1394	0.1399	0.1391	0.2896	0.2886	0.2898
1.80	0.5533	0.5537	0.5535	0.1508	0.1511	0.1506	0.2959	0.2952	0.2960
2.00	0.5388	0.5390	0.5390	0.1609	0.1613	0.1608	0.3003	0.2998	0.3003

Table 3 Comparison of the “computation time” for the two algorithms KMC and MEMC.

Mechanism	Algorithm	Computation time/s	
		$N_0 = 10^5$	$N_0 = 10^6$
(M1) (without reversible steps)	KMC	3	24
	NEKMC	3	32
(M2) (with 3 reversible steps)	KMC	30	292
	NEKMC	4	21

Table 4 Comparison of computation time for the two algorithms KMC and MEMC in stiff conditions.

Mechanism	Algorithm	Computation time/s	
		$N_0 = 10^5$	$N_0 = 10^6$
(M3) ($k_1 = 100 k_2$)	KMC	173	1698
	NEKMC	5	31
(M3) ($k_1 = 1000 k_2$)	KMC	215	2121
	NEKMC	4	18

tions will slow the software. However the NEKMC method is around 11 times faster than KMC method for the (M2) reaction (which has only three reversible steps). One can expect that as the number of the reversible steps increases, the gain in computation time will be greater.

4.2. Rapidity test with reaction (M3) (with stiffness situation)

Most improvement can be observed for the (M3) reaction, with only one reversible step but with stiffness situation. As the differences between the equilibrium constants and the slow step constant increase, the reaction stiffness increases. The computation time augment widely as the reaction stiffness augment. The (M3) reaction is simulated in the stiffness situation mentioned above (where $k_1 = 100k_2$) and in the more stiff situation where $k_1 = 1000k_2$. The computation time obtained for the two algorithms with the values $N_0 = 10^5$ and 10^6 is summarized in Table 4. The NEKMC method is around 34 times faster than KMC method in the less stiff situation when using $N_0 = 10^5$, and 53 times faster when using $N_0 = 10^6$. The improvement is greater in the more stiff situation; which is 53 times faster with $N_0 = 10^5$, and 117 times faster with $N_0 = 10^6$.

We can expect that for more complex reactions with more reversible steps and more stiffness conditions, we will get a greater factor between the computation time in KMC and NEKMC which could attain more than thousands.

5. Conclusion

In this work we substituted the Monte Carlo algorithm (KMC) by the Net-Event Monte Carlo algorithm (NEKMC), which reduces any reversible step in a given mechanism to a single event. By doing so, the total number of events is considerably reduced and the program becomes much faster. The software speed, when using the NEKMC, easily exceeds a hundred times the speed of the KMC algorithm for very simple mechanisms and we can expect that for more complex reactions it will exceed thousands.

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