Monte Carlo Simulation of Stiff Systems of Catalytic Reactions by Sampling Normally Distributed Rate Probabilities

S. Guerrero
Dept. of Chemical Engineering, University of Notre Dame, Notre Dame, IN 46556

E. E. Wolf
Dept. of Chemical Engineering, University of Notre Dame, Notre Dame, IN 46556

DOI 10.1002/aic.11941

Keywords: computer simulations (MC and MD), catalysis, reaction kinetics, surface chemistry/physics

Introduction

In catalytic surface reactions where multiple events of adsorption/desorption/reaction can take place, the time scale of such events can differ significantly from each other, making it challenging when modeling complex surface reactive systems using stochastic methods. In numerical analysis, this is known as the problem *stiffness* and it is characteristic of a system of differential equations with very different eigenvalues. This study introduces a new simple way to deal with stiff problems on reactive catalytic surfaces using a modified kinetic Monte Carlo (KMC) approach. This method is exemplified by solving the Robertson's problem.

Monte Carlo Simulations of Surface Reactions

Monte Carlo methods are advantageous when modeling the kinetics of surface reactions because they permit us to represent the detail structure of the surface. The standard KMC simulations of such systems use individual reaction rates to calculate the probability of the occurrence of each event. Large differences in reaction rates lead to low overall probability of occurrence of events with low rates. Consequently, events with very low probabilities do not occur in the simulation even though in an actual physical system such events do occur. Several approaches having different levels of complexity have been reported in literature to overcome such stiffness using KMC methods.[1–8] A new method is presented in this note to overcome the stiffness problem during MC simulations.

The standard KMC algorithm

Although in most MC simulations, the surface is represented as a two dimensional matrix of surface sites containing a specific structure, here, we follow the more general model developed by Gracia and Wolf,[9,10] which incorporates a third dimension representing a crystallite as a truncated hexagonal pyramid. Three (100) planes having four-fold geometry are located along the walls of the pyramid,[11,12] whereas the top surface layer exhibits a (111) structure. The support is assumed to be a thin square plate with a variable number of crystallites (1–69) randomly distributed onto it. This model permits one to select sites of different activity depending on its location on the crystallite (planes, edges, and basal) and to vary the crystallite size from 8 to 27 Å by changing the number of total atoms that conforms each crystallite. Although the algorithm used in our work uses the surface structure indicated earlier, for the purpose of the calculations presented here all sites are considered to have the same rates. In the KMC algorithm, the simulation starts by initializing all variables and event counters. Then, a crystallite and a site on that crystallite are both randomly chosen. Surface events occur on that site depending on the

---

Correspondence concerning this article should be addressed to E. E. Wolf at ewolf@nd.edu
Current address of S. Guerrero: Center for Advanced Interdisciplinary Research in Materials Sciences - CIMAT - Departamento de Ingeniería Química y Biotecnología, Universidad de Chile, Casilla 2777, Santiago, Chile.

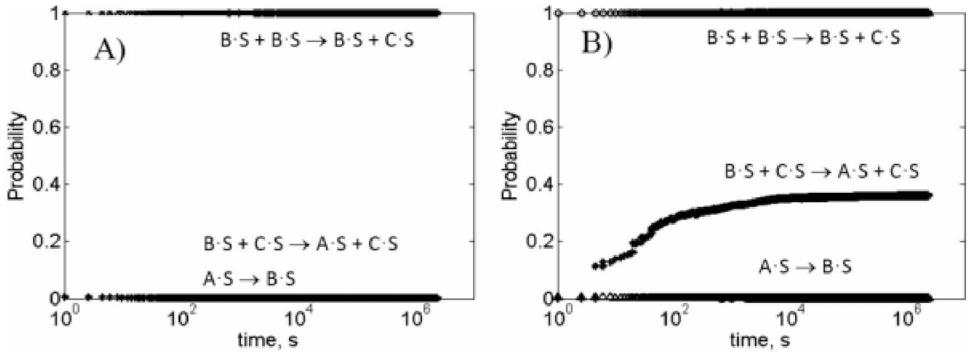

Figure 1. KMC Simulation of the Robertson's problem using the (A) standard cumulative probability calculation and (B) cumulative probabilities calculated from the log-transformed rates.

Each probability is labeled with the corresponding surface reaction rate.

probability of each specific event. Once the event is chosen, another crystallite is selected and the process is repeated until all surface sites are visited, which is referred as a MC iteration. The program iterates many times over the surface until some convergence criteria for surface coverage is met (i.e., steady state). The steady state of the system is checked by monitoring the fluctuation in the number of events during successive iterations. If the fluctuation is below certain percentage, then a steady state has been reached. If the system is not at steady state, the process is repeated again and the algorithm is directed to select a new crystallite and new site. If the steady state has been reached, the algorithm stops. The convergence criteria used here to calculate if the steady state was reached was to achieve 1% of the relative error between the summation of all successful events (considering all crystallites) in the ongoing MC iteration and the last 10 averaged values. In a given iteration, once the status of a site is determined (empty or occupied), the probability of the particular event associated with that site is compared with a random number, α, to decide if the event occurs or not. The calculation of probabilities is discussed later. Every time one of these events occurs, the time is updated and the new state (coverage) of that site is recorded. If the event does not occur, the selection sequence is re-initiated. If the event does take place, the surface is updated and the time is calculated according to the following equation previously used by Fichthorn and Weinberg[13] and others[3]:

$$t = -\ln(\alpha) \Big/ \left(\sum\nolimits_{\mathrm{i}} r_{\mathrm{j}} \right) \tag{1}$$

In Eq. 1, the summation term is over the number of species participating in a surface event having a rate r_i, and $\ln(\alpha)$ is the natural logarithm of a random number α between 0 and 1.

Robertson's problem

This problem consists of an autocatalytic reaction with significant different rates[14] and it is a common example often used as a test problem in numerical studies when comparing stiff integrators.[15] It describes an autocatalytic reaction occurring in three steps: $A \rightarrow B$, $2B \rightarrow C + B$, and $B + C \rightarrow A + C$, having large differences in the magnitude of their rates. As stated by Robertson, the numerical values of the rate constants used in the test problem are $k_1 = 0.04$ (slow reaction), $k_2 = 3 \times 10^7$ (very fast), and $k_3 = 10^4$ (fast). The large differences in the reaction rate constants k_1, k_2, and k_3 determines significant differences in all the reaction rates. If the concentrations of A, B, and C are represented by y_1, y_2, and y_3, then the three reactions can be expressed as a set of differential equations:

$$\frac{dy}{dt} = f(y),\ y(0) = (n, 0, 0)^T, \quad n \in \mathbb{N},\ y \in \mathbb{R}, \quad \text{and} \quad t \in [0, T] \tag{2}$$

$$f(y) = \begin{pmatrix} -0.04y_1 + 10^4 y_2 y_3 \\ 0.04y_1 - 10^4 y_2 y_3 - 3 \cdot 10^7 y_2^2 \\ 3 \cdot 10^7 y_2^2 \end{pmatrix} \tag{3}$$

To solve the Robertson's problem in a stochastic approach, each one of the species A, B, and C is considered as reactants adsorbed on a solid surface (i.e., $A{\cdot}S = \theta_A$, $B{\cdot}S = \theta_B$, $C{\cdot}S = \theta_C$, where S is an active site, the $(\cdot)$ denotes an adsorbed species and θ its coverage). The adsorption/desorption steps are omitted from the reaction sequence to maintain the similarity with the Robertson scheme. At the beginning of the reaction, the surface is assumed to be completely covered by the species A. The species A slowly reacts to produce adsorbed species B with a rate $\Gamma_1 = k_1\theta_A$ ($k_1 = 0.04$). The generated species B reacts very fast with itself to produce the adsorbed species C leaving behind B unreacted. The latter reaction occurs having a rate $\Gamma_2 = k_2\theta_B^2$ ($k_2 = 3 \times 10^7$). The generated species C reacts again with B to re-generate A and leaving the species C unreacted with a rate $\Gamma_3 = k_3\theta_B\theta_C$ ($k_3 = 3 \times 10^4$). The support is assumed to be a thin square plate with four crystallites randomly distributed onto it. The crystallite size used in this simulation was 8 Å with 24 sites exposed on the surface (total of 96 sites) all having the same rates.

Once all the reaction rates have been calculated, they are used to construct a probability distribution. Probabilities are calculated in two different ways: first, we used the standard method in which the probability of an event is calculated as the event rate divided by the sum of the rates of all events (referred hereafter as standard probabilities). The new

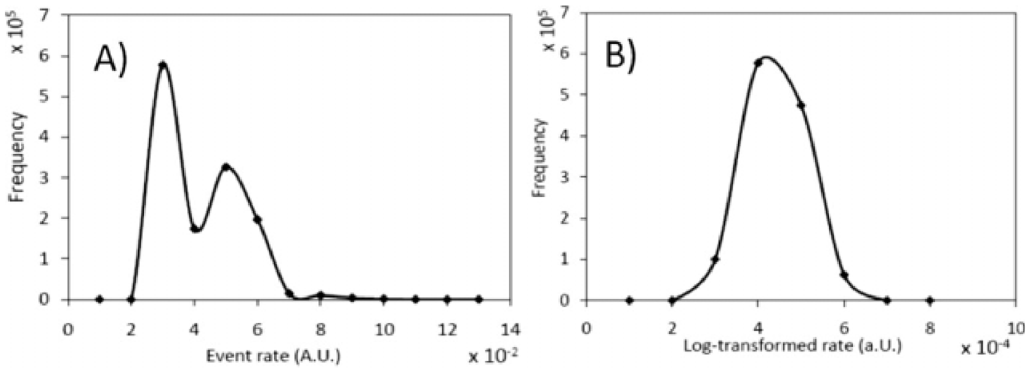

Figure 2. Histogram of the frequencies for the standard and log-transformed rates of decomposition of (A) into (B) in the Robertson's problem.

method introduced here uses the log-transformed rates in the following way:

$$P_i = \frac{\ln(r_i + \varepsilon)}{\sum_i \ln(r_i + \varepsilon)} \tag{4}$$

where P_i is the probability of the i-th event calculated from its log-transformed rate r_i divided by the sum of the log-transformed rates. The value of $\varepsilon = 1$ is added to avoid the calculation of negative probabilities for rates lower than one or invalid values for rates equal to zero. Different values of ε did not affect the simulation results. Probabilities calculated using the log-transformed rates (Eq. 4) will be referred hereafter as logarithmic probabilities (log-KMC). The basis of the log transformation is that it permits to construct a family of normally distributed rates, which are used to build a cumulative distribution function. The latter function is used to obtain the probabilities during iterations. When the data is highly skewed, the logarithmic transformation results in a symmetric normal distribution of the data by reducing the positive skewness, because it compresses the upper end (large event rates) of the distribution (long tail) while stretching out the lower end (low event rates). This basically occurs because the distances between 0.1 and 1, 1 and 10, 10 and 100, etc., are the same in a logarithmic scale. Probabilities are easily calculated and compared in a log-transformed way, no matter the order of magnitude of the rates, and any skewness of the data is eliminated under a log transformation.

In the Roberson problem, because the rate constants of each reaction step differ by several orders of magnitude, the standard probabilities of the slow events would be very small while others would be close to one. The standard probabilities for every event in the Robertson's problem are shown in Figure 1A as a function of time. The results shows that the probability of the reaction of B with itself (the autocatalytic step) is dominant during all iterations ($2B \geq C + B$), whereas the probability of the other two reactions is very low. It is evident that under these conditions, the MC simulations would result in a steady coverage of species A (the surface start initially covered by A). The other events would simply not occur because of their low probability. This result is inaccurate when compared with the nonstochastic solutions. To be able to account for the occurrence of low probability events, the way the probabilities are calculated must be modified. Figure 1B shows that when applying the log transformation to the rates involved in the Robertson's problem, the probabilities calculated by Eq. 4 are well distributed within 0–1 range. Since now not all the events have a negligible probability, the log transformation also decreases the number of null events and saves computational time.

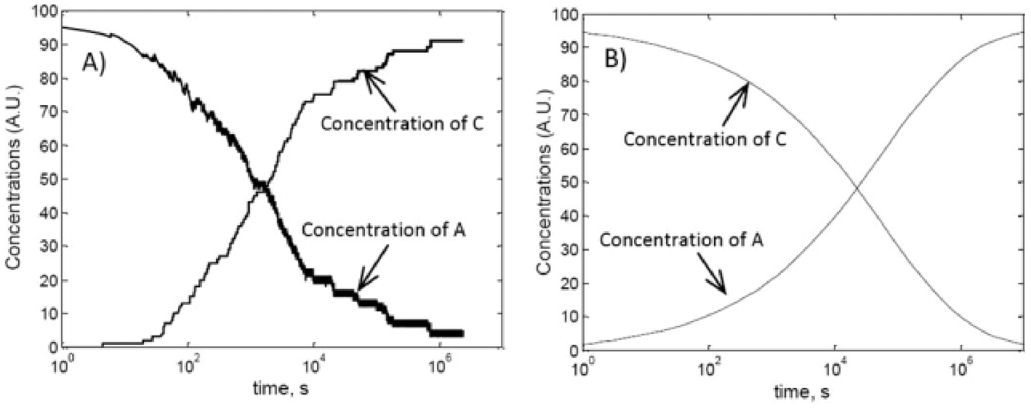

Figure 3. Concentration profile from the solution of the Robertson's equation using the (A) log-KMC method and (B) the exact solution calculated by a Runge–Kutta algorithm. The initial value of (A) was set to 96 (*n* in Eq. 2).

A histogram of frequencies vs. the event rates for the reaction of A to form B (Figure 2A) clearly shows that the rates follow a bimodal distribution and it is left skewed. The logarithmic distribution of probabilities for the decomposition of A into B in the Robertson's problem, displayed in Figure 2B, shows a bell-shaped distribution closed to a normal distribution of the log-transformed rates. The same analysis for all the events, results in a family of normally distributed variables that when used to build a probability distribution during iterations allows sampling of the low rate events.

The surface concentrations obtained using the log-KMC probabilities of the Robertson problem (Figure 3A) are comparable with the results obtained by solving the numerical problem using a Runge–Kutta integration (Figure 3B). It can be seen that the log-KMC method captures the behavior of the numerical solution and that it converges to a steady state value. The shift in the concentrations profile observed in Figure 3A by using the log-KMC can be due to the discrete manner of solving the problem and to the use of a discrete mesh (crystallites). When the standard KMC method was used, the large differences on the magnitude of the rates and the low probability of the reaction of A to B led to the absence of any reaction on the surface. Clearly, the log-KMC method is capable of circumventing the stiffness of the Robertson's problem when using stochastic methods.

Conclusions

In some catalytic reactions, the large differences in time scales of some reactions lead to stiff problems not easy to be solved by stochastic MC methods. This work demonstrates a new and simple method to construct probabilities from the reaction rates no matter the degree of stiffness of the problem. The method denoted here as log-KMC applies a logarithmic transformation of the rates to calculate the probabilities of all events. The autocatalytic reaction system known as the Robertson's problem was solved, and it was shown that the log-KMC method is efficient in obtaining solutions of a stiff problem. This simple method has the potential to be widely used in the solution of stiff problems and it is not restricted to chemical reaction on surfaces. Further work using the new log-KMC method used in a Monte Carlo simulation of the preferential oxidation of CO in the presence of hydrogen will illustrate the advantage of using this method.

Acknowledgments

The support of this work by a Bayer Postdoctoral Fellowship in Environmental Chemistry through the Center for Environmental Science and Technology at the University of Notre Dame is gratefully acknowledged.

Literature Cited

1. He J, Zhang H, Chen J, Yang Y. Monte Carlo simulation of kinetics and chain length distributions in living free-radical polymerization. *Macromolecules*. 1997;30:8010–8018.
2. Gillespie DT. Approximate accelerated stochastic simulation of chemically reacting system. *J Chem Phys*. 2001;115:1716–1733.
3. Vlachos DG. Stochastic modeling of chemical microreactors with detailed kinetics–induction times and ignitions of H_2 in air. *Chem Eng Sci*. 1998;53:157–168.
4. Snyder MA, Chatterjee A, Vlachos DG. Net-event kinetic Monte Carlo for overcoming stiffness in spatially homogeneous and distributed systems. *Comput Chem Eng*. 2005;29:701–712.
5. Resat H, Wiley HS, Dixon DA. Probability-weighted dynamic Monte Carlo method for reaction kinetic simulations. *J Phys Chem B*. 2001;105:11026–11034.
6. Trushin O, Karim A, Kara A, Rahman TS. Self-learning kinetic Monte Carlo method: application to Cu(111). *Phys Rev B (Condens Matter Mater Phys)*. 2005;72:115401:1–9.
7. Haseltine EL, Rawlings JB. Approximate simulation of coupled fast and slow reactions for stochastic chemical kinetics. *J Chem Phys*. 2002;117:6959–6969.
8. Rao CV, Arkin AP. Stochastic chemical kinetics and the quasi-steady-state assumption: application to the Gillespie algorithm. *J Chem Phys*. 2003;118:4999–5010.
9. Gracia F, Wolf EE. Monte-Carlo simulation of the effect of crystallite size on the activity of a supported catalyst. *Chem Eng J*. 2001; 82:291–301.
10. Gracia FJ, Wolf EE. Non-isothermal dynamic Monte Carlo simulations of CO oxidation of Pt supported catalysts. *Chem Eng Sci*. 2004;59:4723–4729.
11. Mavrikakis M, Stoltze P, Nørskov JK. Making gold less noble. *Catal Lett*. 2000;64:101–106.
12. Dulub O, Hebenstreit W, Diebold U. Imaging cluster surfaces with atomic resolution: the strong metal-support interaction state of Pt supported on TiO_2(110). *Phys Rev Lett*. 2000;84:3646–3649.
13. Fichthorn KA, Weinberg WH. Theoretical foundations of dynamical Monte Carlo simulations. *J Chem Phys*. 1991;95:1090–1096.
14. Robertson HH. The solution of a set of reaction rate equations. In: Walsh J, editor. *Numerical Analysis: An Introduction*. Washington, DC: Thompson Book Company INC, 1966;178–182.
15. Hairer E, Wanner G. *Solving Ordinary Differential Equations. II. Stiff and Differential-Algebraic Problems*, 2nd ed. Springer-Verlag, Germany, 1996.

Manuscript received Nov. 28, 2008, and revision received Apr. 1, 2009.