PRACTICAL STOCHASTIC MODEL FOR CHEMICAL KINETICS

Leonardo Silva-Dias and Alejandro López-Castillo*
Departamento de Química, Universidade Federal de São Carlos, 13560-970 São Carlos – SP, Brasil

A) EXAMPLES OF STOCHASTIC SIMULATION

A.1 PSM Scheme

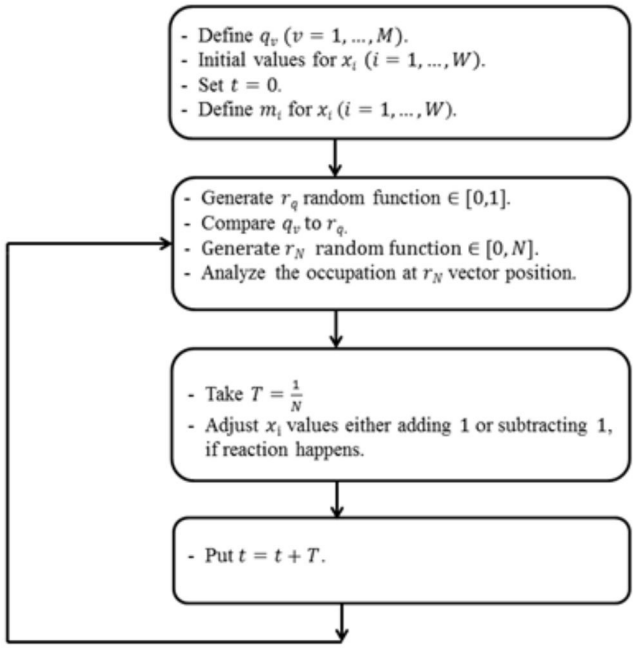

Figure 1S. *PSM Scheme: q_v are the reaction rate constants for v different reactions (v = {1, …, M}); x_i are different chemical species (i={1, …, W}); t is the time; m_i is the "factor m" for different chemical species. r_q is a random number that belongs to [0,1]; r_N is a random number that belongs to [1, N], which defines a specific position inside the vector; N is the size of vector. T=1/N is the additional time and t=h/N, where h is the number of Monte Carlo steps*

A.2 Zhdanov model for the Brusselator system

Zhdanov[1S] considers, in brief, the following Monte Carlo steps to solve the Brusselator system:

a) Define the kinetic constants as normalized probabilities p_1, p_2, p_3, and p_4, and diffusion constants $p_X{}^d$ and $p_Y{}^d$, where $p_X{}^d = 1 - p_1 - p_2$;
b) A circular matrix is filled partially with *X* and *Y* particles;
c) Positions pos_n, and probabilities *p*, are randomly selected;
d) If pos_1 is empty and $p<p_4$, *X* appears in this position, i.e., $A \rightarrow X$;
e) If pos_1 is filled with *X* and $p<p_1$, *X* is exchanged by *Y* at same position, $X \rightarrow Y$;
f) If $p_1<p<p_1+p_2$, *X* is exchanged by *E* in pos_1, $(X \rightarrow E)$;
g) Or else *X* is diffused with an $ap_X{}^d$ probability, $X \rightarrow X$;
h) If pos_1 is filled with *Y*, a new position pos_2 is obtained randomly;
i) If pos_2 is empty and $p<p_1$, *Y* is diffused with an $ap_Y{}^d$ probability, $Y \rightarrow Y$;
j) If pos_2 is filled with *Y*, the processes stop;
k) If pos_2 is filled with *X*, a new position for pos_3 is obtained randomly;
l) If pos_3 is filled with *X*, then *X* must appear at pos_1 for $p<p_3$, $2X+Y \rightarrow 3X$;
m) For other situations, the process breaks.

The trace of a stability matrix for a Brusselator system is given by $T = p_1B - p_2 - p_3(p_4A/p_2)$.[2S] If $B=A=1$ (inferred), and is considering the values of *p*'s in reference,[1S] then the trace is $T=0.00275 > 0$, i.e., the system is unstable and oscillation can happen when mediated by a limit cycle. In this model, *B* must be $B \leq 1$, *T* is limited to $T < 1$ for $p_1 \sim B \sim 1$ and $p_2 \sim p_3(p_4A/p_2)^2 \sim 0$ with $p_3(p_4A)^2 << p_2{}^2$. *T* is $T = B - 1 - A^2$ for *p*'s = 1. The PSM can consider any value of *T*, in particular, $T>1$.

A.3 PSM: $A \rightarrow B \leftrightarrow C$ reaction

An example of the stochastic method is given by the $A \rightarrow B \leftrightarrow C$ system. The *A* compartment (or vector) with, e.g., $N=10$ positions, was considered totally filled, and the *B* and *C* compartments were empty. The initial configuration is shown in Figure 3S for $h=0$ (0^{th} Monte Carlo step). The compartments can have any occupation from 0 to *N*. For example, a compartment with 400 "particles" and $N=1000$ positions has a dilution $d=0.4$. A random simulation for an $A \rightarrow B \leftrightarrow C$ system for several Monte Carlo (*h*) steps is shown in Figure 2S.

The necessary steps to simulate the $A \rightarrow B \leftrightarrow C$ reaction with $N=10$ are:

a) To randomly select a number from 1 to 10; if the position at the same selected number in the *A* compartment is occupied (by a "particle"), then its "particle" disappears at this place. The *B* compartment acquires a particle at the same number position with a unitary of *q* probability. Non-unitary probabilities of *q* could be considered; a unitary one was used to simplify this discussion.
b) To randomly select a second number from 1 to 10; if the position at the same selected number in the *B* compartment is occupied, then its "particle" disappears. That "particle" appears at the same number position in the C compartment with a *q'* probability.
c) To randomly select a third number from 1 to 10; if the position at the same selected number in the *C* compartment is occupied, then this place loses its "particle". Since the reaction $B \leftrightarrow C$ is reversible, the *B* compartment gets that "particle" at the same number position with a *q"* probability.
d) After these steps above, the three-step-procedure is reinitiated and repeated until it reaches equilibrium or a steady state.[3S]
e) When the position corresponding to a randomly selected number is empty, no reactions occur, but the time flow follows.

h=0	A	B	C	h=25	A	B	C	h=50	A	B	C	h=100	A	B	C
1	•			1		•		1			•	1			•
2	•			2		•		2		•		2		•	
3	•			3			•	3		•		3			•
4	•			4			•	4			•	4		•	
5	•			5		•		5		•		5			•
6	•			6			•	6			•	6			•
7	•			7		•		7		•		7		•	
8	•			8	•			8		•		8		•	
9	•			9			•	9		•		9			•
10	•			10		•		10		•		10		•	

Figure 2S. *The Erhenfest Urn model for an $A \rightarrow B \leftrightarrow C$ reaction with N=10 at several Monte Carlo steps: h=0; 25; 50; 100, respectively*

*e-mail: alcastil@ufscar.br

B) STOCHASTIC AND DETERMINISTIC CONNECTIONS: TIME FLOW

The stochastic and deterministic time flow connections obtained from a first order reaction of $A \rightarrow B$; the stochastic (with N_A=N=300) and the deterministic solutions are presented in Figure 3S.

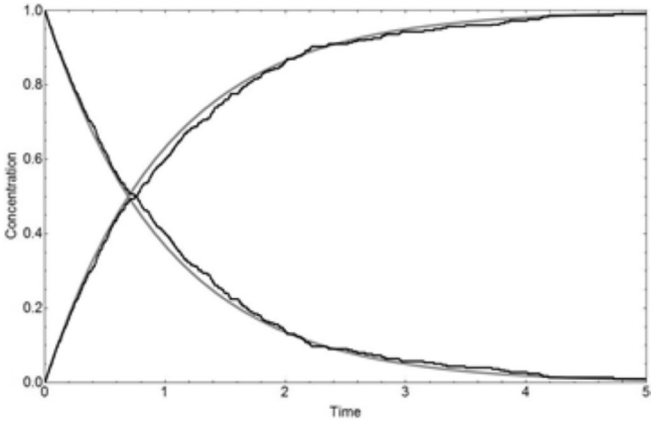

Figure 3S. *Relative concentrations of A and B as a function of time for the $A \rightarrow B$ reaction with N_A=N=300. The deterministic solution (the smooth line) is also shown*

The first order half-life is $t_{1/2} = \ln 2/k \approx 0.69315$ and is comparable to the following examples: a) N = 40 corresponds to $h_{1/2}$ = 29 and consequently $t_{1/2} = h_{1/2}/N$ =29/40 = 0.725; b) N = 100 gives $h_{1/2}$ = 56 with $t_{1/2}$ = 0.56; c) N = 10000 gives $h_{1/2}$ = 6924, $t_{1/2}$ = 0.6924. These results indicate that the true flow of time can be given by t = h/N.

The following analytical deterministic solutions were considered: a) for the first order reaction $A \rightarrow B$: $[A](t) = [A]_0 \exp(-k\,t)$, where $[A]_0$ is the initial concentration of the A and k kinetic and is constant with a half-life time $t_{1/2}$=ln2/k; b) for the second order reaction ($A + B \rightarrow C$): $[A](t) = [B](t) = 1-[C](t) = 1/(1+2t)$ with $[A]_0$=$[B]_0$, $[A]_0$=$[B]_0$=1, and $t_{1/2}$=1/(k $[A]_0$)=1 with unitary kinetic constants.

The second order reaction of $A + B \rightarrow C$ was simulated with a stochastic model similar to the first order reaction. Two random numbers were selected, one for the A compartment and the other for B. If the positions in A and B at the selected random numbers are filled, two "particles" disappear in the A and B compartments and are "transformed" into the other "particle" in compartment C. The stochastic and determinist simulations of the second order reaction of $A+B \rightarrow C$ with N_A=N_B=N=500 and k = $t_{1/2}$=1 are shown in Figure 4S:

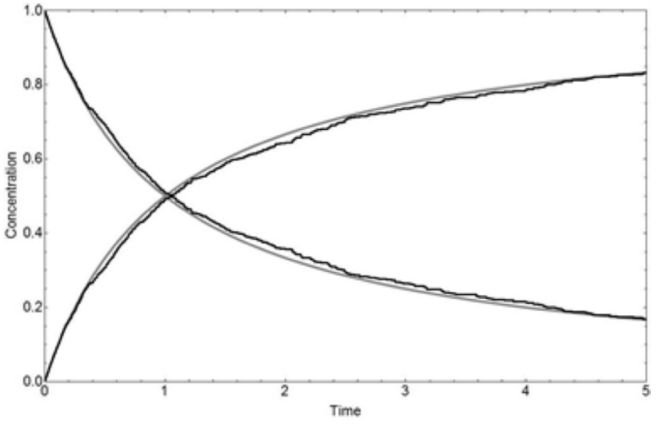

Figure 4S. *Relative concentrations of A (or B) and C as a function of time for the second order reaction of $A+B \rightarrow C$ with N_A=N_B=N=500 and $k = t_{1/2}$=1. The deterministic solution (the smooth gray line) is also shown*

C) STOCHASTIC AND DETERMINISTIC CONNECTIONS: ABSOLUTE CONCENTRATIONS

The concentration of the A specie in the reaction $A+X \rightarrow Y$ is given by $[A] = mN_A/N$, where N_A is the number of A particles, N is the size of the compartment, and m is the rate of the reaction enhancement.

If N_A = 900, N = 1000 and m=2, the concentration is $[A] = mN_A/N$ = 2 × 900/1000 = 1.8, which is equivalent to N_A = 600, N = 1000, m=3, and $[A]$ = 3 × 600/1000 = 1.8. The theoretical half-times, for the reaction of $A+X \rightarrow Y$, is $t_{1/2} = \ln 2 / ([A]\,k) \approx 0.385$ with $[A]$ = 1.8 and k = 1. The numerical half-times obtained from the PSM with $[A]$ = 1.8 and $N = N_X$ = 1000 are: $h_{1/2}$ = 407 ± 25 for N_A = 600 and m=3; $h_{1/2}$ = 358 ± 30 for N_A = 900 and m=2, where the absolute fluctuation (error) is given by $N^{1/2}$ (the relative fluctuation is $N^{-1/2}$). These results are shown in Figure 5S.

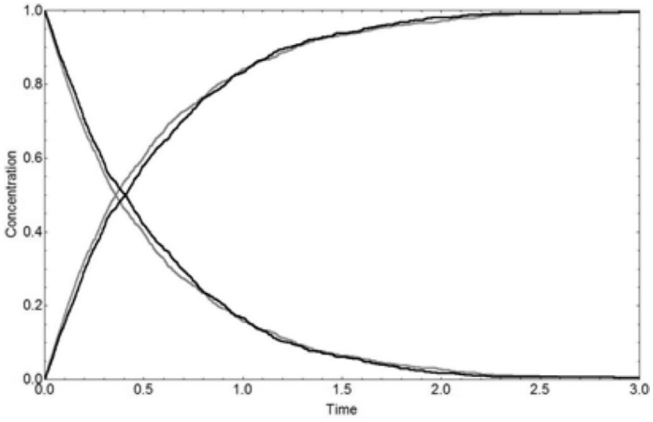

Figure 5S. *[X] and [Y] as a function of the time for the reaction of $A+X \rightarrow Y$ with N=1000, N_X=1000, N_A=900, and m=2 (gray lines) — and with N_A=600 and m=3 (black lines)*

D) FORTRAN CODE PROGRAM FOR THE LOTKA SYSTEM

```
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C          Monte Carlo - Lotka
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION X(100000),Y(100000),A(100000)
      INTEGER s, xJ
C     Number of Particles
      Np=10000
      Nx=10000
      Ny=10000
      Na=10000
      Xacumula=0
      Yacumula=5000
C     probabilities
      q1=0.5
      q2=0.6
      q3=0.7
C-----------------------------------------------
C      Factor "m" (specie A)
       ma=4
C-----------------------------------------------
      idum=1
C-----------------------------------------------
C     Number of Steps
      Nj=400000
```

```
C-------------------------------------------
C     Counter
      NXYZ=0
C-------------------------------------------
C      Variables Looping
       XX= (Nx+Xacumula)/Nx
       YY= (Ny+Yacumula)/Ny
C      Accumulators
       Acomx= Xacumula/Nx
       Acomy= Yacumula/Ny

C-------------------------------------------
C     Vectors
      DO 101 I=1,Np
          X(I)=0
          Y(I)=0
          A(I)=0
101   CONTINUE
C-------------------------------------------
C      Filling Vectors
       DO 100 I=1,Nx
97        N6=ran(idum)*Np+1
          IF(X(N6).eq.1)GOTO 97
          IF(X(N6).eq.0)X(N6)=1
100    CONTINUE
       DO 300 I=1,Ny
99        N7=ran(idum)*Np+1
          IF(Y(N7).eq.1)GOTO 99
          IF(Y(N7).eq.0)Y(N7)=1
300    CONTINUE
       DO 350 I=1,Na
98        N8=ran(idum)*Np+1
          IF(A(N8).eq.1)GOTO 98
          IF(A(N8).eq.0)A(N8)=1
 350   CONTINUE
C-------------------------------------------
C      Print of Initial Conditions
       NsomaA=Na
       NsomaX=Nx
       NsomaY=Ny
       Xt=NsomaX+Xacumula
       Yt=NsomaY+Yacumula
       Nzero=0

       WRITE(10,*)Nzero,Xt/Np
       WRITE(11,*)Nzero,Yt/Np
C-------------------------------------------
C     Beginning of Steps
      DO 200 xJ=1,Nj
C-------------------------------------------
C       Defining mx
        XX= (Xacumula+NsomaX)/NsomaX
        mx= XX
        xmf= XX-mx
        Acomx=Acomx+xmf
        mAc= Acomx
        mx=mx+mAc
        Acomx=Acomx-mAc
C-------------------------------------------
C       Defining my
        YY= (Yacumula+NsomaY)/NsomaY
        my= YY
        ymf= YY-my
        Acomy=Acomy+ymf
        mAcc= Acomy
        my=my+mAcc
        Acomy=Acomy-mAcc
C-------------------------------------------
C      X+Y--->2Y
       DO 121 m1=1,mx
       DO 122 m2=1,my
C      Random Choices
       N1=ran(idum)*Np+1
       N2=ran(idum)*Np+1
C-------------------------------------------
C      Constant of Velocity
C      In this reaction constant q1
       XY=ran(idum)
       WRITE(15,*)XY
       IF(XY.lt.q1)THEN
C-------------------------------------------
        IF((X(N1).eq.1).and.(Y(N2).eq.1))THEN
        IF(Xacumula.gt.0) then
        Xacumula=Xacumula-1

        else
        X(N1)=0
        endif
          NsomaY=0
          DO 23 k=1,Np
            NsomaY=NsomaY+Y(k)
23        CONTINUE
         IF (NsomaY.eq.Np)THEN
         Yacumula=Yacumula+1
         ELSE
2        NYr=ran(idum)*Np+1
         IF(Y(NYr).eq.1)GOTO 2
         IF(Y(NYr).eq.0)Y(NYr)=1
      ENDIF
      ENDIF
      ENDIF
122   CONTINUE
121   CONTINUE

C-------------------------------------------
C       Defining mx
        XX= (Xacumula+NsomaX)/NsomaX
        mx= XX
        xmf= XX-mx
        Acomx=Acomx+xmf
        mAc= Acomx
        mx=mx+mAc
        Acomx=Acomx-mAc
C-------------------------------------------
C       A + X---> 2X
C-------------------------------------------
      DO  115 m=1,ma
      DO  116 m3=1,mx
C     Random Choice
         N3=ran(idum)*Np+1
         N4=ran(idum)*Np+1
C-------------------------------------------
C      Constant of Velocity
C      In this reaction constant q2
       XYY=ran(idum)
       IF(XYY.lt.q2)THEN
```

```
C-------------------------------------------
        IF((A(N4).eq.1).and.(X(N3).eq.1))THEN
           A(N4)=0
4          NAr=ran(idum)*Np+1
           IF(A(NAr).eq.1)GOTO 4
           IF(A(NAr).eq.0)A(NAr)=1
            NsomaX=0
            DO 24 k=1,Np
            NsomaX=NsomaX+X(k)
24         CONTINUE
          IF (nsomaX.eq.Np)THEN
              Xacumula=Xacumula+1
          ELSE
3           NXr=ran(idum)*Np+1
            IF(X(NXr).eq.1)GOTO 3
            IF(X(NXr).eq.0)X(NXr)=1
          ENDIF
          ENDIF
          ENDIF
116     CONTINUE
115    CONTINUE

C-------------------------------------------
C       Defining my
        YY= (Yacumula+NsomaY)/NsomaY
        my= YY
        ymf= YY-my
        Acomy=Acomy+ymf
        mAcc= Acomy
        my=my+mAcc
        Acomy=Acomy-mAcc
C-------------------------------------------
C       y --> P
       DO 123 s=1,my
C      Random Choice
       N5=ran1(idum)*Np+1
C-------------------------------------------
C       Constant of Velocity
C       In this reaction constant q3
       XYYY=ran(idum)
       IF(XYYY.lt.q3)THEN
C-------------------------------------------
        IF(Y(N5).eq.1) THEN
        IF(Yacumula.gt.0) then
        Yacumula=Yacumula-1
        ELSE
        Y(N5)=0
        endif
        ENDIF
        ENDIF
123    continue
```

```
C-------------------------------------------
CC      Adding
        NsomaX=0
        NsomaY=0
        NsomaA=0
          DO 22 k=1,Np
             NsomaA=NsomaA+A(k)
             NsomaX=NsomaX+X(k)
             NSomaY=NsomaY+Y(k)
22         CONTINUE
      Xt=Xacumula+NsomaX
      Yt=Yacumula+NsomaY
      XXX=Xt/Np
      YYY=Yt/Np
C     Converting xJ Integer to xxJ Real
      xxJ=xJ
      YXZ=xxJ/Np
C     Printing at kp steps
      kp=10
      NXYZ=NXYZ+1
      If(NXYZ.eq.kp) then
          WRITE(10,355)YXZ,XXX
          WRITE(11,355)YXZ,YYY
          WRITE(13,*)YXZ,NsomaA
          WRITE(14,355)XXX,YYY
      NXYZ=0
      endif
355   FORMAT(3(F24.10))
200   CONTINUE
      WRITE(6,*)'finished'
      STOP
      END
```

REFERENCES

1S. Zhdanov, V. P.; *Phys. Chem. Chem. Phys.* **2001**, *3*, 1432.

2S. Prigogine, I.; Nicolis, G.; *Self-Organization in Non-Equilibrium Systems: From Dissipative Structures to Order through Fluctuations*, 1ª ed., John Wiley & Sons: New York, **1977**. p.499.

3S. Souza-Filho J. C.; Lopez-Castillo, A.; *Quim. Nova* **2007**, *30*, 1759.