DYNAMICAL MONTE CARLO SIMULATIONS

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INTRODUCTION

The Monte Carlo method as a numerical integration method is efficient at obtaining steady state or equilibrium solutions to the studied systems. Its results are normally reported as integral values over inherently time dependent systems. However it can also be used in the study of the dynamical behavior of systems, and its application to dynamical and time dependent systems is worthy of wide investigation.

The cooperative behavior and dynamics of collections of constituents of matter generating structural and configuration properties are often not amenable to a macroscopic continuum description, and their discrete nature must be accounted for. Molecular Dynamics simulations are used in this situation to describe the trajectories and orbits of the individual nucleons, nuclei, atoms or molecules on potential energy surfaces. However, Molecular Dynamics methods are computationally incapable of considering large systems of interacting particles.

Monte Carlo methods, in terms of dynamics, are capable of bridging the gap between the microscopic formulations, which are computationally incapable of dealing with large collections of particles such as the individual ions and electrons in a plasma, and the macroscopic formulations which do not realistically represent the discreteness of the systems at hand. The way this is achieved in Dynamical Monte Carlo is by adopting a coarse grained approach to the problem considering aggregates of particles representing average features which arise from microscopic behavior.

DYNAMICAL MONTE CARLO

A successful implementation of Dynamical Monte Carlo depends upon the adoption of a sampling procedure in which any transition probabilities from one state of the simulated system to another are based on a realistic dynamical model of the underlying physical phenomenon. The Monte Carlo technique has not been widely applied to time dependent phenomena. Instead, the results of clearly time dependent situations are reported as integral values, restricting the possibility of comparison to theory and to actual experimental results. This needlessly has so far restricted the wide use of the technique.

A clear relationship between the Monte Carlo simulation time and real time must be established in a given simulation for an effective treatment of time by Monte Carlo methods. The establishment of this relationship is clear within the class of problems covered by the theory of Poisson's processes. Within that theory, static and dynamic properties of Hamiltonian systems can be simulated with a clear correspondence between the simulation time and real time. Adequate treatment of a system's dynamical behavior in real time requires that we clearly define the relationship between the Monte Carlo calculational time step and the transition probabilities of the system.

A Poisson process is a process with two states such as forward and reverse or occupied and vacant. One can consider a situation from Chemical Physics. It could, for instance, represent the time dependence of the occupancy or vacancy of a given site in an adsorption and desorption equilibrium of a solid single crystalline surface with a gas phase collection of molecules.

A random variable X has a Poisson distribution if its probability density function with parameter λ is given by:

$$P(\lambda) = \frac{\lambda^x e^{-\lambda}}{x!}, \quad x = 0,1,...; \lambda > 0 \tag{1}$$

If the time intervals between events are sampled from the exponential probability density function:

$$e^{\frac{1}{\lambda}} = e^{-\lambda},$$

then the number of events occurring in an unit interval of time is from the Poisson distribution P(λ).

Let us consider the random variable N that counts the number of events occurring within a time period t. The probability that n events will happen within the time interval t is given by the Poisson's distribution with x=n, and λ=rt:

$$P(N = n) = \frac{(rt)^n}{n!} e^{-rt} \tag{2}$$

where: r is the rate at which a certain event occurs.

The expected number of events occurring within a time interval t and the variance in the Poisson distribution is equal to λ, resulting in:

$$\overline{N} = \lambda = rt \tag{3}$$

Thus a series of random, independent events occurring at an average rate r is a Poisson's process.

The probability density function of the time between successive events is here given by the exponential distribution:

$$f(t) = re^{-rt} \tag{4}$$

From the probability density function f(t), one can calculate the mean time, or mathematical expectation of the time between events as:

$$\bar{t} = \int_0^\infty tre^{-rt} dt = \frac{1}{r} \tag{5}$$

In particular, we consider in that context the time dependence and the attainment of a Langmuir adsorption and desorption equilibrium in a lattice surrounded by a gas system, as discussed by Fichthorn and Weinberg.

We first seek an analytical solution to the problem in terms of time behavior, then develop the Dynamical Monte Carlo procedure that would reproduce the theoretical result. This would enlighten us as to the conditions under which such a dynamic simulation can be successfully undertaken.

THEORY OF LANGMUIR ADSORPTION AND DESORPTION EQUILIBRIUM

The kinetic expression for the process of adsorption and desorption is described in terms of the fractional surface coverage T as:

$$\frac{dT}{dt} = r_a(1-T) + r_d T \qquad (6)$$

where: r_a is the adsorption random average rate [site.sec]$^{-1}$,

r_d is the desorption random average rate [site.sec]$^{-1}$.

We assume that the adsorbate and desorbate do not interact. If r_a and r_d are known from the properties of the system under consideration, we can solve the last equation analytically as follows.

We expand the right hand side of Eqn. 6:

$$\frac{dT}{dt} = r_a - (r_a - r_d)T$$

Separating the variables and multiplying by an integrating factor:

$$e^{(r_a+r_d)t},$$

turns the left hand side into a complete integral:

$$\frac{d}{dt}[T\ e^{(r_a+r_d)t}] =$$

$$e^{(r_a+r_d)t}\ \frac{dT}{dt} + (r_a + r_d)Te^{(r_a+r_d)t} =$$

$$r_a e^{(r_a+r_d)t}$$

Integrating with respect to time yields:

$$\int_0^t d[T.e^{(r_a+r_d)t}] = \int_0^t r_a e^{(r_a+r_d)t} dt$$

$$Te^{(r_a+r_d)t} - T_0 = \frac{r_a}{r_a + r_d}[e^{(r_a+r_d)t} - 1]$$

Solving for T(t) and assuming that its initial value at time t=0 is zero, we get:

$$T(t) = \frac{r_a}{r_a + r_d}[1 - e^{-(r_a+r_d)t}] \quad (7)$$

The equilibrium value is obtained as the time t tends to infinity as:

$$T(\infty) = \frac{r_a}{r_a + r_d} \quad (8)$$

The procedure for the calculation of the result of Eqs. 7 and 8 is shown in Fig. 1. A plot of T(t) is generated in Fig. 2, for r_a=2.0 and r_d=1.0, leading to an equilibrium vale of T as 2/3. The analytical value is to be compared later to the results of the Dynamic Monte Carlo procedure.

```
!       Program Dynamical__Monte_Carlo_Analytical for
!       Calculates analytical solution for Dynamical Monte Carlo benchmark
!       M. Ragheb
!       program Dynamical_Analytical
        dimension theta(101),t(101)
!       theta=fractional surface coverage
!       t=time [seconds]
        real theta,t,rd,ra,dt,z,xx
        integer n
!       Time Scale
        d=5.0
!       Number of time steps
        n=100
!       Time nodes
        dt=d/n
        t(1)=0.0
        do i=2,n+1
                t(i)=(i-1)*dt
        end do
!       Average desorption rate, rd [site.second]-1
        rd=1.0
!       Average  adsorption rate, ra [site.second]-1
        ra=2.0
!       Open output file for visualization in Excel
        open (unit=10,file='profile.xls',status='unknown')
!       Calculate solution at different time steps
        z=t(1)
        call sol(z,xx,rd,ra)
        theta(1)=xx
        write(10,*) theta(1),t(1)
        write(*,*) theta(1),t(1)
```

```
        do i=2,n+1
                z=t(i)
                call sol(z,xx,rd,ra)
                theta(i)=xx
                write(10,*) theta(i),t(i)
                write(*,*) theta(i),t(i)
        end do
        end
!       Define solution
        subroutine sol(z,xx,rd,ra)
        real z,xx,rd,ra
        c=ra/(ra+rd)
        xx=c*(1.0-exp(-(ra+rd)*z))
        return
        end
```

Figure 1. Analytical solution procedure for estimating the fractional surface coverage as a function of real time, $r_{adsorption}$ = 2 [site.sec]$^{-1}$, $r_{desorption}$ = 1 [site.sec]$^{-1}$.

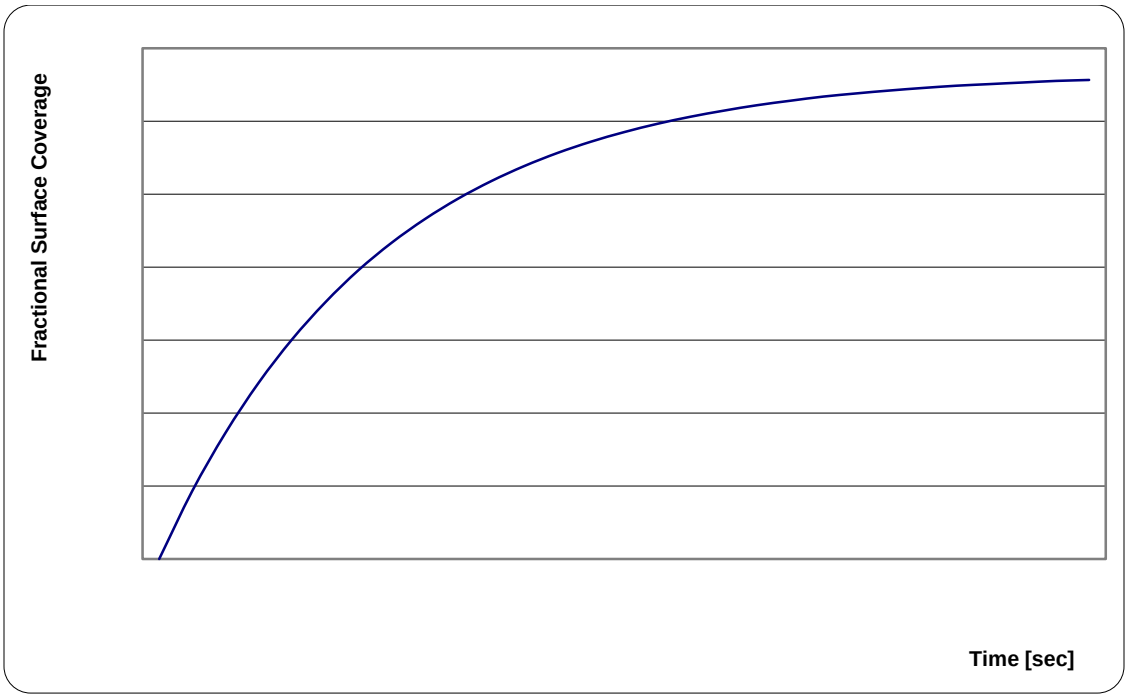

Figure 2. Analytical results for fractional surface coverage as a function of time, $r_{adsorption}$ = 2 [site.sec]$^{-1}$, $r_{desorption}$ = 1 [site.sec]$^{-1}$.

MONTE CARLO PROCEDURE

A flow diagram describes the Dynamical Monte Carlo procedure in Fig. 3, and the procedure itself is shown in Fig. 4. We begin by defining a square lattice containing in our case 128x128 adsorption or desorption sites. This lattice is originally empty. We also initialize the number of trials and the real elapsed time counters.

The following transition probabilities are defined for the two states of adsorption and desorption:

$$W_i = \frac{r_i}{\sup\{r_i\}} \tag{9}$$

That is, the transition probabilities are normalized to the one with largest value among them. In our simulation, $r_a > r_d$, implying that $\sup\{r_i\} = r_a$, and:

$$\begin{aligned} W_a &= \frac{r_a}{r_a} = 1 \\ W_d &= \frac{r_d}{r_a} \end{aligned} \tag{10}$$

By comparison with a pseudo random number uniformly distributed over the interval [0,1], these transition probabilities are sampled at each sampled site. If the site is unoccupied, the adsorption transition probability is sampled to decide whether the site becomes occupied by an adsorbed particle. If the site is occupied, the desorption transition probability is sampled to decide whether the occupied site should be desorbed.

To assure the correct correspondence between the Monte Carlo simulation time and real time, after each desorption or adsorption, the simulation time is incremented by sampling a time from the exponential distribution. If no desorption or adsorption occur, the time is not sampled, but the history counter is incremented, and a new site is sampled on the lattice.

The sampling of time is done using the parameter:

$$r_i = (n - m_i) r_a + m_i r_d \tag{11}$$

where: n is the total number of available sites on the lattice,

m_i is the number of occupied sites at the i-th trial.

Obviously the occupation ratio at trial i is estimated to be plotted as a function of time as:

$$T_i = \frac{m_i}{n} \tag{12}$$

We now sample the exponential probability density function of Eqn. 4. We first construct a cumulative distribution function then equate it to a pseudo random number uniformly distributed over the unit interval:

$$c(t) = \int_0^t r e^{-rt} dt = 1 - e^{-rt} = \rho \tag{13}$$

We invert the cumulative distribution function, and substitute the value of the parameter r from Eq. 11, and substitute (1-ρ_I) by ρ_i since they are equally distributed, and this saves a computational step as:

$$t_i = -\frac{1}{r_i}\ln(1-\rho_i)$$
$$= -\frac{1}{r_i}\ln\ \rho_i \qquad (14)$$
$$= \frac{1}{(n-m_i)r_a + m_i\, r_d}\ln(\rho_i), \qquad i = 1,2,3,\ldots$$

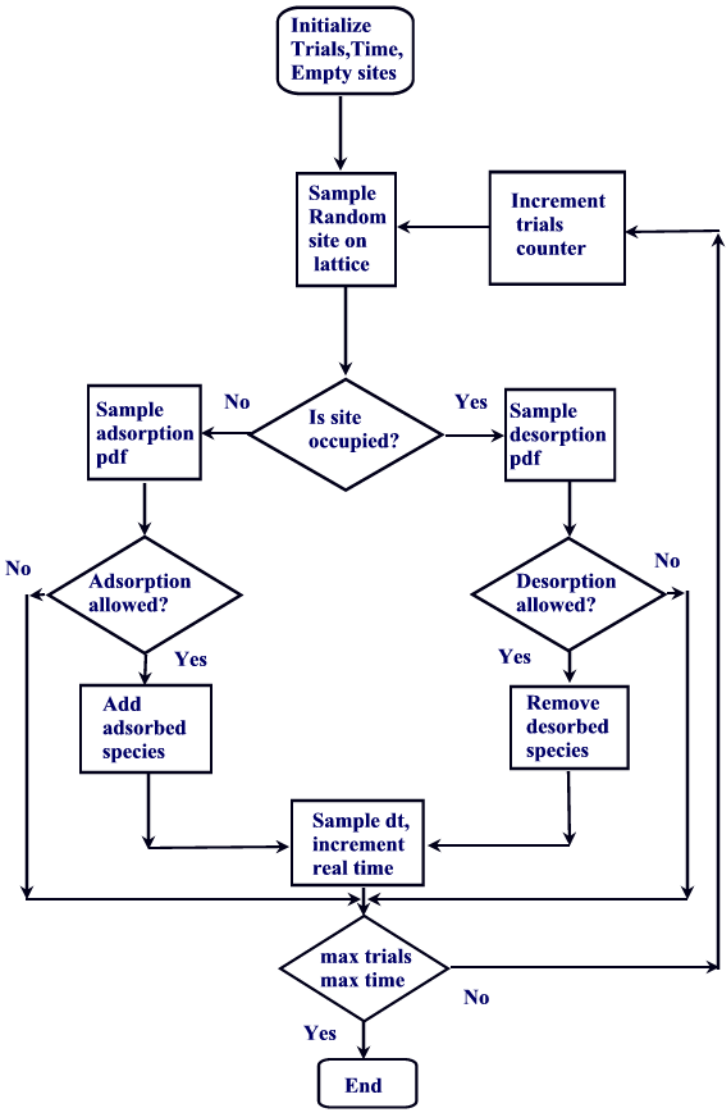

Figure 3. Flow Chart for Dynamical Monte Carlo Procedure.

This sampled value of time is incremented in the real time counter to estimate the real time of the process being simulated.

One must be careful in the choice of a random number generator that generates a long period of pseudo random numbers. A generator with a short repeating period will lead to erroneous results, in that it will not fully sample the phase space of interest to us.

```
!!      Program Dynamical__Monte_Carlo for
!       Dynamical Monte Carlo simulation
!       M. Ragheb, University of Illinois at Urbana-Champaign,2/8/2003
        program Dynamical_Monte_Carlo
        dimension theta(100001),t(100001)
        dimension lattice(128,128)
!       theta=fractional surface coverage
!       t=time [seconds]
        real theta,t,rd,ra,wd,wa,dt,xm,xn
        integer n,nnn,lattice,trials,maxtrials,ii,jj,k
!       Total number of lattice sites
        nnn=128
        n=nnn*nnn
        xn=n
!       Set total number of trials
        maxtrials=100000
!       Set maximum simulation time
        maxtime=2.5
!       Average desorption rate, rd [site.second]-1
!       rd=2.0
        rd=1.0
!       Average  adsorption rate, ra [site.second]-1
!       ra=1.0
        ra=2.0
!       Transition probabilities are defined by normalization
!       to the largest of the adsorption or desorption rates: ra or rd.
!       Desorption transition probability
!       wd=rd/rd
        wd=rd/ra
!       Adsorption transition probability
!       wa=ra/rd
        wa=ra/ra
!       Open output file for visualization of fractional surface coverage
!       as a function of elapsed time in Excel
        open (unit=10,file='profile.xls',status='unknown')
!       Open output file for visualization of lattice coverage
!       in Array Visualiser
        open (unit=11,file='array.agl',status='unknown')
!       Initialize empty lattice, empty site=0, occupied site=1
        do i=1,nnn
                do j=1,nnn
                        lattice(i,j)=0
                end do
        end do
!       Initialize time index
        k=1
!       Initialize fractional surface coverage
        theta(k)=0.0
!       Initialize time
        t(k)=0.0
!       Initialize number of trials
        trials =1
!       Sample a random site on the lattice
999     continue
```

```
            call random(rr)
            ii=(nnn+1)*rr
            if (ii.LT.1) ii=1
            call random(rr)
            jj=(nnn+1)*rr
            if (jj.LT.1) jj=1
!           Check whether site is occupied or not
!           Lattice site not occupied
            if (lattice(ii,jj).LE.0) then
!           Sample adsorption process
                  call random(rr)
!           Add a species at the lattice site
                  if (rr le.wa) then
                        lattice(ii,jj)=1
                        goto 30
                        else
!           Do not increment time
                        goto 888
                  end if
            end if
!           Lattice site occupied
20          if (lattice(ii,jj).GT.0) then
!           Sample desorption process
                  call random(rr)
!           Remove species from lattice site
                  if(rr.LE.wd) then
                        lattice(ii,jj)=0
                        goto 30
                        else
!           Do not increment real time
                        goto 888
                  end if
            end if
30          continue
!           Calculate fractional surface coverage theta
            xm=0.0
            do i=1,nnn
                  do j=1,nnn
                        if (lattice(i,j).GT.0)then
                              xm=xm+1.0
                        end if
                  end do
            end do
            theta(k)=xm/xn

!           Write solution at each time step
            write(10,*) theta(k),t(k)
!           Calculate exponential distribution parameter r
            r=(xn-xm)*ra + xm*rd
!           Sample time increment from exponential distribution
            call random(rr)
            dt=-log(rr)/r
            write(*,*) trials,k,theta(k),t(k)
!           Increment time
            k=k+1
            t(k)=t(k-1)+dt
!           Increment number of trials
888         trials=trials + 1
!           Test for maximum number of trials
            if ((trials.LT maxtrials).or.(t(k).LT.timemax)) then
                  goto 999
            end if
```

```
!       Write lattice state at end of simulation
        do i=1,nnn
                write(11,77)(lattice(i,j), j=1,nnn)
77      format(128i5)
        end do
        stop
        end
```

Figure 4. Dynamical Monte Carlo Procedure.

SIMULATION RESULTS

For an initially empty lattice, Fig. 5 shows the Dynamical Monte Carlo simulation of the fractional surface coverage T(t)of the adsorbate as a function of real time t. The simulation result converges to the expected theoretical value of 2/3 at a real time of about 1.4 seconds. The agreement between the simulation result and the exact analytical result of Fig. 2 is remarkable.

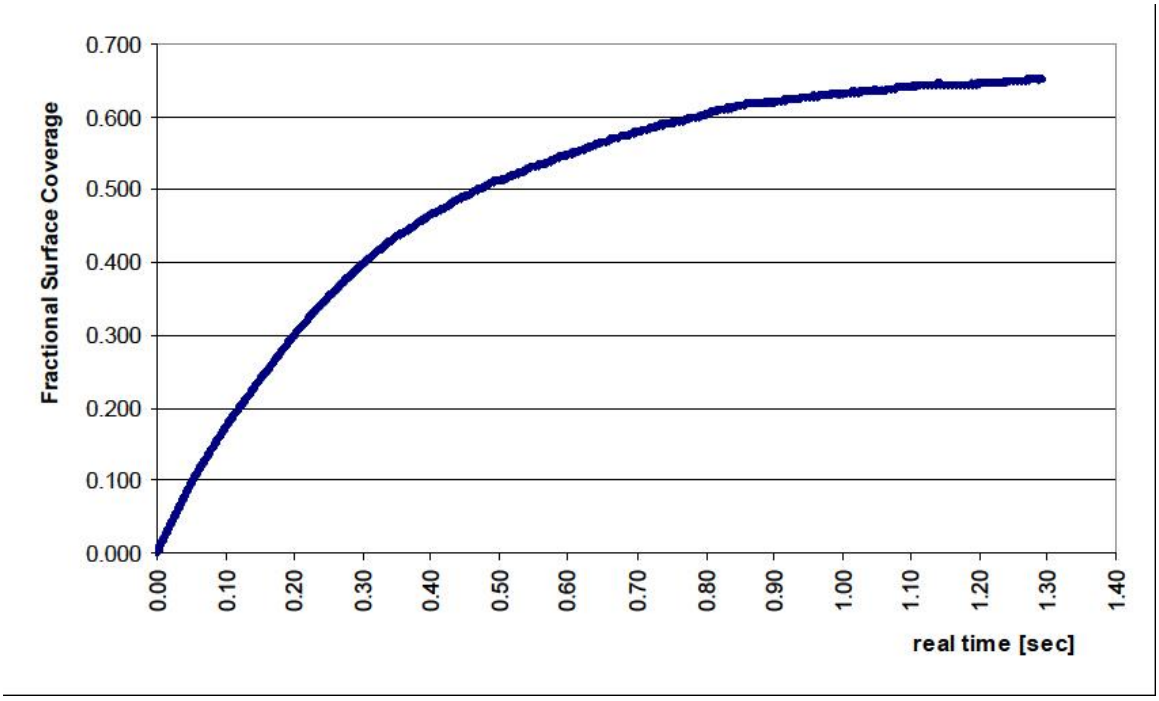

Figure 5. Monte Carlo Simulation results for fractional surface coverage as a function of real time, $r_{adsorption}$ = 2 [site.sec]$^{-1}$, $r_{dewsorption}$ = 1 [site.sec]$^{-1}$.

The dynamic behavior of the system can further be watched on the road to equilibrium in Figs. 6-10, which display the occupied lattice sites as the number of simulations increases from 10 to 10,000 by factors of 10 at a time. The lattice is initially unoccupied but the sites where the simulated gas molecules get adsorbed increase as the number of simulations increases. Eventually, the fractional surface coverage attains the theoretical value of 2/3 for this case, and remains at this equilibrium value.

DISCUSSION

The Langmuir adsorption and desorption process treated above is a special case of a large class of problems generally described by the Master equation:

$$\frac{\partial P(\bar{s},t)}{\partial t} = \sum_{\bar{s}'} T(\bar{s}' \rightarrow \bar{s})\, P(\bar{s}',t) - \sum_{\bar{s}} T(\bar{s} \rightarrow \bar{s}')\, P(\bar{s},t)$$

(16)where: s and s' are successive states of the system,

P(s,t) is the probability that the system is at state s at time t,

T(s'→s) is the transition probability per unit time of the system undergoing a transition from state s' to state s.

A successful implementation of Dynamical Monte Carlo to this class of problems depends upon the following criteria:

1. Adoption of a sampling procedure in which any transition probabilities from one state of the simulated system to another are based on a realistic dynamical model of the underlying physical phenomenon.
2. A clear relationship between the Monte Carlo simulation time and real time must be established in a given simulation for an effective treatment of time by Monte Carlo methods. Adequate treatment of a system's dynamical behavior in real time requires that we clearly define the relationship between the Monte Carlo calculation time step and the transition probabilities of the system.
3. The events describing the systems should be independent within the framework of a Poisson process.

According to Feller, other Poisson's processes are encountered in different areas of applications:

1. The process of radioactive transformations or decay,
2. Chromosomes interchanges in biological cells,
3. Telephone connections to a wrong number,
4. Bacterial colonies growth and decay,
5. Blood counting procedures.

The Monte Carlo technique has not been widely applied to time dependent phenomena even though, by its treatment of aggregates, it fills an important gap between continuum and microscopic simulation methods. Instead, the results of clearly time dependent situations are usually reported as integral values, restricting the possibility of comparison to theory and to actual experimental results. This needlessly has so far restricted the wide use of the technique.

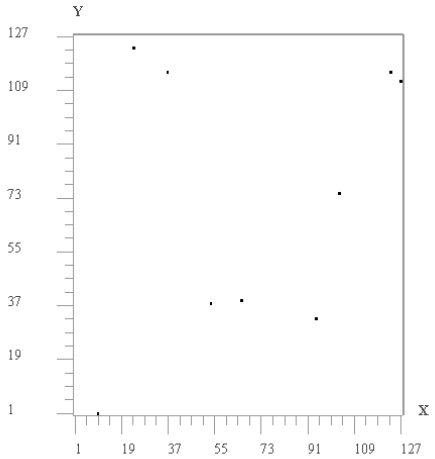

Figure 6. Adsorption sites in dynamic Monte Carlo Simulation. Number of trials = 10.

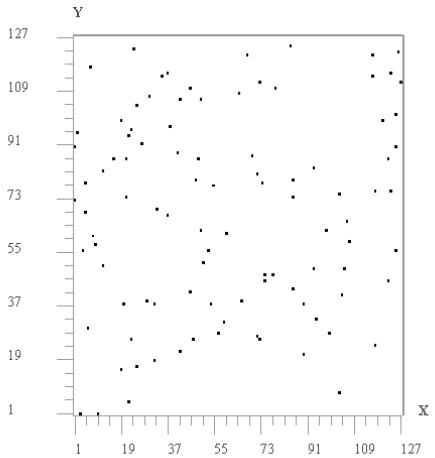

Figure 7. Adsorption sites in dynamic Monte Carlo Simulation. Number of trials = 100.

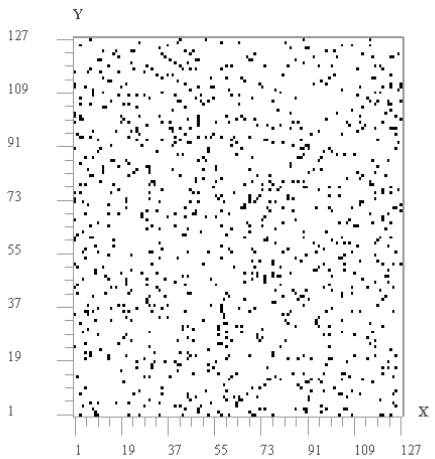

Figure 8. Adsorption sites in dynamic Monte Carlo Simulation. Number of trials = 1000.

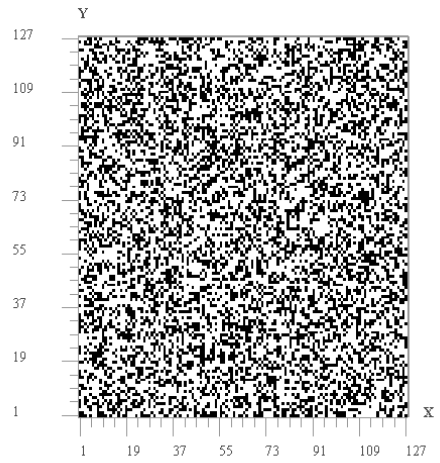

Figure 9. Adsorption sites in dynamic Monte Carlo Simulation. Number of trials = 10,000.

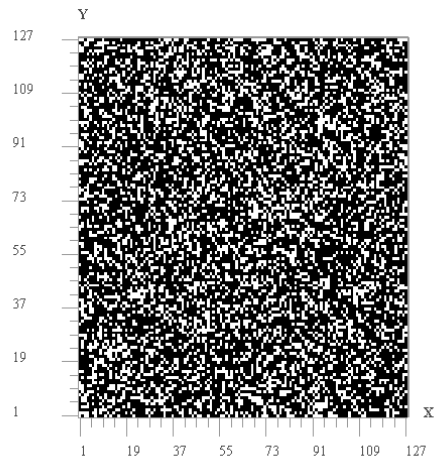

Figure 10. Adsorption sites in dynamic Monte Carlo Simulation. Number of trials = 100,000.

EXERCISES

1. Simulate the problem of Langmuirian adsorption equilibrium with the following adsorption and desorption rates:

$$r_a=1.0\ [\text{site.sec.}]^{-1}\ ,\ r_d=2.0\ [\text{site.sec.}]^{-1},$$

implying the following adsorption and desorption transition probabilities:

$$W_a=r_a/r_d=1/2, \text{ and } W_d=r_d/r_d=1.0.$$

Compare the attained equilibrium to the theoretical value.

2. A special case of the adsorption equilibrium problem is the process of producing an isotope under neutron irradiation in a nuclear reactor. Simulate the process of attaining the equilibrium activity. In this case the adsorption term is replaced by an isotope creation term, and the desorption term is replaced by a term describing the radioactive

decay of the produced isotope. Upon removal of the isotope from the reactor, only the radioactive decay term becomes active, and the activation term becomes zero. Simulate the buildup of the isotope upon neutron irradiation in the reactor, then its subsequent decay upon withdrawal from the reactor core.

3. Use different size lattices e.g. 16, 32, 64, 128, 256, to study the effect of the number of simulated adsorption, desorption sites on the convergence to equilibrium in terms of computational time needed.

4. The production and decay of reactor neutron poisons such as Samarium and Xenon, affect the control of nuclear reactors, reaching equilibrium values during reactor operation at a constant power level. This equilibrium is affected by power fluctuations that can cause severe power transients. Upon shut down, Xenon in particular initially increases, and then decays after reaching a maximum, leading to a reactor dead time in the range of 24 hours where the reactor cannot be restarted unless special provision to override the Xenon peak are initially incorporated in the original design. Try developing a Dynamical Monte Carlo procedure that would be useful in studying the Xenon and Samarium power fluctuation effects.