

## CHAPTER 4

### MONTE CARLO METHOD

The Monte Carlo method was developed by von Neumann, Ulam, and Metropolis at the end of Second World War to study the diffusion of neutrons in fissionable material. The name *Monte Carlo*, chosen because of the extensive use of random number in the calculations, was coined by Metropolis in 1947 [2].

The Monte Carlo simulations are widely used to study the microscopic properties of the solution, such as structural and energetic properties, based on the knowledge of potential function; e.g. to study, how a solute influences the solvent structure or how a solute is solvated by solvent molecules in the solution. Such structural and energetic informations are very difficult to obtain from spectroscopic measurements, especially in dilute solutions.

In this chapter, the principles of the general Monte Carlo method and the Metropolis scheme will be presented together with conditions of calculations and calculating procedures, including evaluation of the simulated results such as radial distribution functions and integration numbers.

#### 4.1 Principles of Monte Carlo Method

The principle of Monte Carlo calculations under consideration are based on pair potential functions, implementing the assumption that only two body forces are to be considered, i.e., linear additivity is given for the total configurational energy  $E(v)$  of the system, containing  $N$  particles, can be written thus as a sum of pair-wise interaction energies between the individual particles  $E_{ij}(v)$  of the system.

$$E(\mathbf{v}) = \sum_{i>j}^{N(N-1)/2} E_{ij}(\mathbf{v}) \quad (4.1)$$

where  $\mathbf{v}$  is a configurational coordinate of the particles in the system.

Average of any property of interest  $\langle F \rangle$  of an  $N$ -particles system determine under canonical ensemble conditions with volume  $V$  at a constant temperature  $T$  can be written as

$$\langle F \rangle = \frac{\int \dots \int F(\mathbf{v}) \exp(-E(\mathbf{v})/kT) d\mathbf{v}}{\int \dots \int \exp(-E(\mathbf{v})/kT) d\mathbf{v}} \quad (4.2)$$

where  $d\mathbf{v}$  denotes a volume element in three dimensional phase space. If the starting configuration is generated randomly in three dimensional space, integration over many orders of magnitude would be needed for the integrand  $\exp(-E(\mathbf{v})/kT)$ , shown in eq.(4.2). This is the principle of the general Monte Carlo method which is, however, not practicable.

## 4.2 Metropolis Monte Carlo Method

The above principle was modified by Metropolis et al. in 1953 [2] based on the idea of importance sampling. In this method, the  $N$  configurations are randomly generated but accepted with respect to their probability,  $P(\mathbf{v})$ , and they are evenly weighted with  $P(\mathbf{v})$ . After taking a quite large number of space point  $M$ , eq.(4.2), can be approximated by the sum

$$\langle F \rangle \cong \bar{F} = \frac{\sum_{i=1}^M F_i(\nu) P_i(\nu)^{-1} \exp(-E(\nu)/kT)}{\sum_{i=1}^M P_i(\nu)^{-1} \exp(-E(\nu)/kT)} \quad (4.3)$$

The probability  $P(\nu)$  in Metropolis Monte Carlo method is given by a Boltzmann factor:

$$P_i(\nu) = \exp(-E(\nu)/kT) \quad (4.4)$$

then eq. (4.3) can be reduced to a simple expression of

$$\langle F \rangle = \frac{1}{M} \sum_{i=1}^M F_i \quad (4.5)$$

where  $F_i$  denotes the value of the property  $F$  of the system after the  $i$ th configurational change.

## 4.3 Conditions of Calculations

### 4.3.1 Simulation Cube

The cubic box is duplicated throughout space to form an infinite lattice. It contains all investigated particles. This box simply forms a convenient axis system for measuring the particles. The length of the cubic box  $L$  (Å), which contains  $N_i$  particles for  $m$  species, can be calculated as

$$L^3 = \frac{\sum_{i=1}^m N_i M_i}{0.602D} \quad (4.6)$$

where  $D$  denotes the experimental density of the solution in  $\text{g/cm}^3$  at the temperature and pressure which the simulations have been carried out;  $M_i$  is the ionic or atomic weight of species  $i$ .

### 4.3.2 Optimal Number for Particles

Number of particles in the investigated system has been limited by the computer efficiency. The larger number of particles, the higher accuracy of the simulated results, and the longer CPU time required for the simulations. It has been found that optimal number of the particles is approximately 200.

### 4.3.3 Starting Configuration

The starting configuration in the Monte Carlo simulation of all particles has often been generated randomly. However, the particle should be distributed homogeneously so that the system will be equilibrated easier. Therefore, the shortest distance between particles,  $l_{\min}$ , can be approximated by

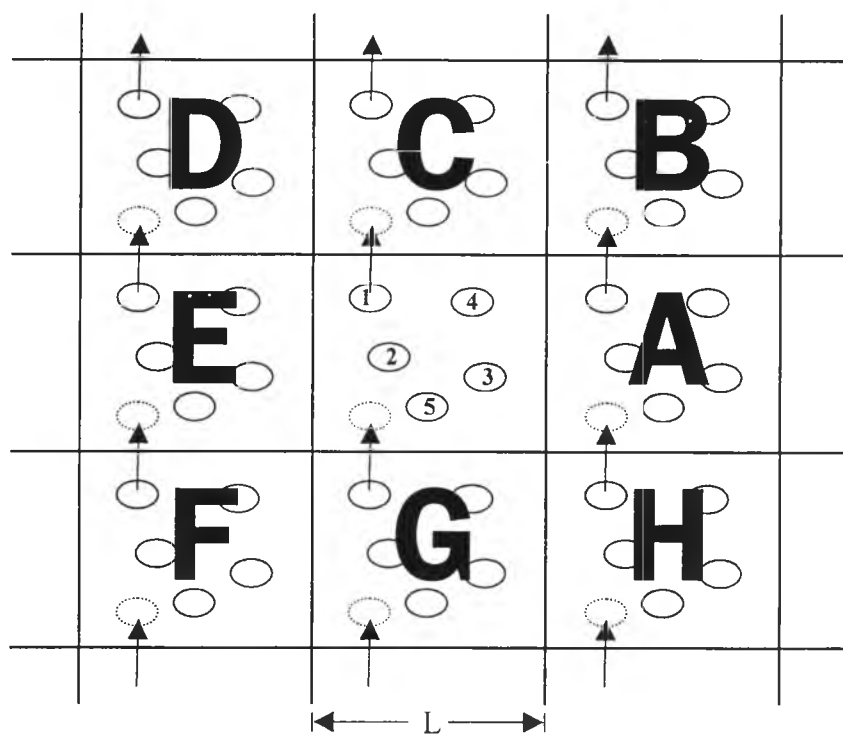
$$l_{\min} = \sqrt[3]{\frac{L^3}{N}} \quad (4.7)$$

#### 4.3.4 Periodic Boundary Condition

An idea of the computer simulation is to enhance the ability of small systems to represent properties of large systems. The *infinite* system is usually simulated by using of the *periodic boundary condition*, which is required in order to keep the constant density. This condition leads to an infinite array of identical cubes in three dimensions, the basic cube is surrounded by an infinite number of image cubes which have the same configuration and each cube contains a certain number,  $N$ , of molecules, as illustrated in a two-dimensional picture in Figure 4.1.

In the simulation, as a molecule moves in the original box, its periodic image in each of the neighbouring boxes moves in exactly the same way. Thus, as a molecule leaves the central box, one of its images will enter through the opposite face. There are no walls at the boundary of the central box, and no surface molecules. This box simply forms a convenient axis system for measuring the coordinates of the  $N$  molecules. The duplicate boxes are labeled A, B, C, etc. As particle 1 moves through a boundary, its images,  $1_A$ ,  $1_B$ , etc. (where the subscript specifies in which box the image lies) move across their corresponding boundaries. The number density in the central box (and hence in the entire system) is conserved. It is not necessary to store the coordinates of all images in a simulation (an infinite number), just that of the molecules in the central box. When a molecule leaves the box by crossing a boundary, attention may be switched to the image just entering.

If a small number of particles were confined in an isolated finite cube to the surface of the cube, the proportion of the surface compare to particles inside would be much higher than in real systems. Therefore, this would not be a suitable description for a macroscopic sample, so called *surface effect*. The need of introducing the periodic boundary condition is caused by the need to avoid this effect.



**Figure 4.1** A two-dimensional periodic.

#### 4.3.5 Minimal Image Convention

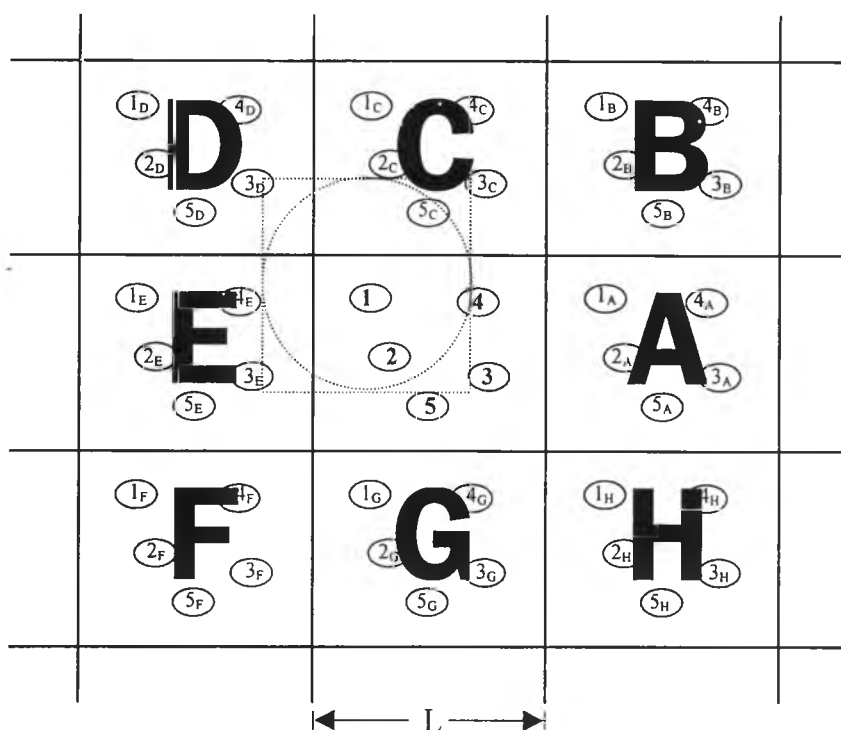
The most time consuming in the Monte Carlo simulation involves the calculation of the potential energy of a particular configuration. To calculate contributions to the potential energy involving molecule 1, one assume pair-wise additivity. The interaction between molecule 1 and every other molecule  $i$  in the simulation box must be included. There are  $N-1$  terms in this sum (see eq. (4.1)). However, in principle the interaction between molecule 1 and images  $i_A, i_B, i_C$ , etc. lying in the surrounding boxes must be included as well. This is an infinite number of terms, and of course it is impossible to calculate in practice. For a short-range potential energy function, an approximation may be used to restrict this summation. Consider molecule 1 to rest at the center of a region which has the same size and

shape as the basic simulation box. Molecule 1 interacts with all the molecules whose centers lie within this region that is with the closest periodic images of the other  $N-1$  molecules. This is called the *minimal image convention*: for example, in Figure 4.2, molecule 1 interacts with molecules 2 and  $5_c$ . This technique, which is a natural consequence of the periodic boundary condition, was first used in simulations by Metropolis et al [2].

#### 4.3.6 Spherical Cut-Off

In the minimal image convention, the calculation of the potential energy due to pair-wise additive interactions involves  $N(N-1)/2$  terms. This may still be a very substantial calculation for a system of 1,000 particles. A further approximation significantly improves this situation. The largest contribution to the potential comes from neighbours close to the molecule of interest, and for short-range interactions, a spherical cut-off can be applied. This means setting the pair potential  $E(r_{ij})$  to zero for  $r_{ij} \geq r_c$ , where  $r_c$  is the cut-off distance. The dashed circle in Figure 4.2 represents this cut-off, and in this case molecules 2 and  $5_c$  contribute to the interaction with 1, since their centers lie inside the cut-off, whereas molecule  $2_c$  does not contribute. In a cubic simulation box of side  $L$ , the number of neighbours explicitly considered is reduced by a factor of approximately  $4\pi r_c^3/3L^3$ , and this may be a substantial saving. The introduction of a spherical cut-off could be a perturbation, and the cut-off distance should be sufficiently large to ensure that this perturbation is very small.

The cut-off distance must be no greater than  $L/2$  for consistency with the minimal image convention, and it is applicable only to rapidly decreasing potential terms, e.g.  $1/r^{12}$  or exponential terms.



**Figure 4.2** The minimal image convention in a two-dimensional system.

#### 4.3.7 Long-Range Interactions

A long-range interaction is defined as one in which the spatial interaction falls off no faster than  $r^{-d}$  where  $d$  is dimensionality of the system. In another meaning, long-range interaction is one in which all the particles lying outside the cut-off sphere of a given particle. The charge-charge, charge-dipole, dipole-dipole, and charge-quadrupole interactions are the examples of such a strong interaction. Long-range interactions are a serious problem for the computer simulation, since their range is greater than half the box length. So far, *the Ewald sum* [30,45] and *the reaction field method* [30,46] have been two widely used methods, which can be employed to handle the problem of long-range interaction. The Ewald sum procedure, which is perfectly consistent with periodic boundary conditions, is a



technique for efficiently summing the interaction between a particle and all its periodic image. The reaction field method introduced without the assumption of the periodicity is to treat all molecules beyond the cut-off sphere of radius from a center as forming a continuum with a given dielectric constant; therefore, any charge lying inside the cut-off sphere will polarize the continuum and create a reaction field at the center.

#### 4.4 Calculating Procedures

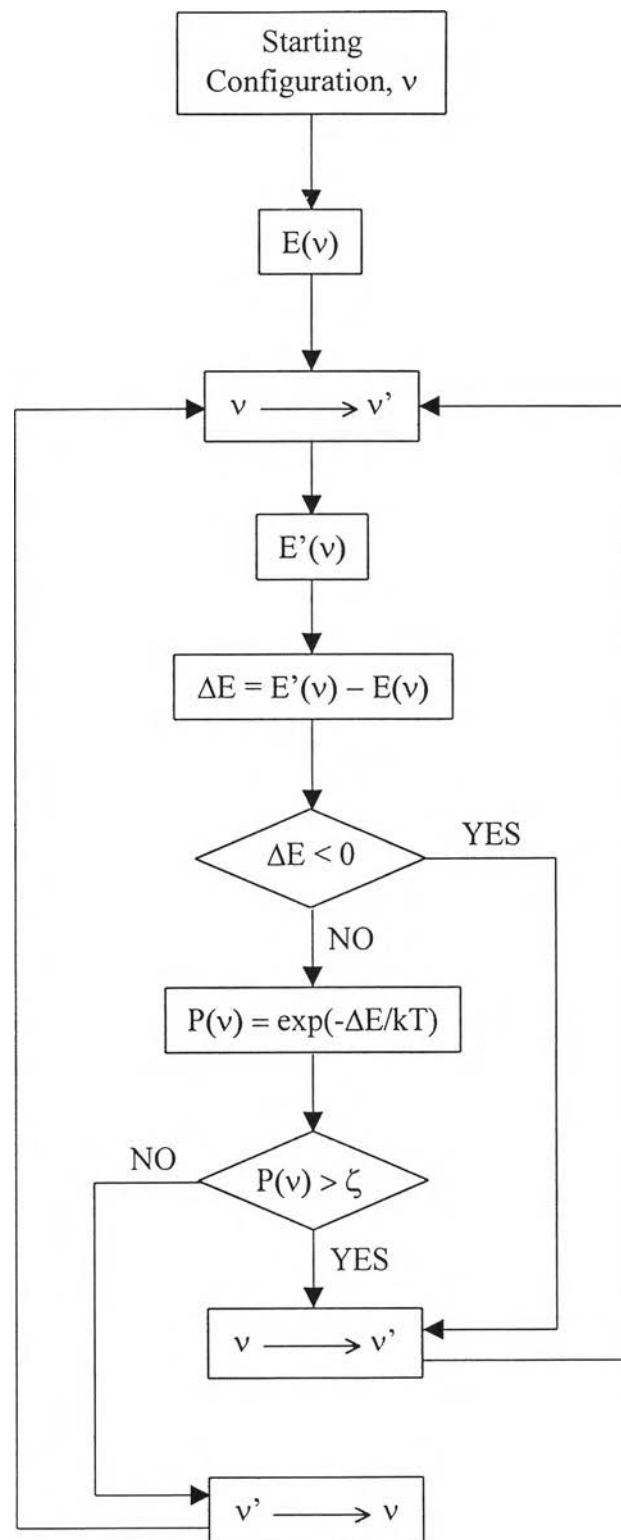
Consider a system consisting of  $N$  particles in a basic cube of side length  $L$  at  $T$  Kelvin with infinite cube periodicity, the Monte Carlo algorithm consists essentially in iterating the following steps which are illustrated in Figure 4.3. A summary of procedures, which are carried out, is the following.

- 1.) Determine an initial configuration,  $v$ , that is chosen by which the position of the  $N$  particles are generated randomly or from a previous simulation.
- 2.) The computer then calculates the interaction energy,  $E(v)$ , of this configuration according to eq. (4.1) based on the potential function.
- 3.) The computer chooses randomly an integer from 1 to  $N$  and the particle will be determined to move. Then move the labeling particle,  $v \rightarrow v'$ , in succession according to the following prescription:

$$X \rightarrow X + \delta_x$$

$$X \rightarrow Y + \delta_y$$

$$Z \rightarrow Z + \delta_z$$



**Figure 4.3** The calculating steps of Monte Carlo simulations.

where  $\delta_x$ ,  $\delta_y$ ,  $\delta_z$  are the maximum allowed displacement, which for the sake of this argument is arbitrary. The maximal allowed displacement must be chosen with some cares. If it is too large, most of the moves will be forbidden. If it is too small, to configuration will not change enough. In either case it will take longer to reach equilibrium. If the particles are moved to a new position, one at a time, and a sphere after such a move happens to overlap with another sphere. The particle will be returned to its original position, and repeat this step.

If the move carried the particle outside the basic cube, it is brought back to the other side according to the boundary condition.

4.) Calculate interaction energy of the new configuration,  $E'(v)$ , and the change in different energy  $\Delta E$  between the new and the old configurations, which is caused by the move

$$\Delta E = E'(v) - E(v) \quad (4.8)$$

The next step is to determine  $\Delta E$ . There are two cases to consider:

- 4.1) If the move is downhill in energy ( $\Delta E < 0$ ), then probability of state  $v$  is greater than state  $v'$  and would bring the system to a state of lower energy and the new configuration is accepted.
- 4.2) If the move is uphill in energy ( $\Delta E > 0$ ), the move which is accepted with a probability  $P(v)$ , can be readily expressed as the Boltzmann factor of the energy difference (see eq. (4.4)).

To accept a move with a probability of  $\exp(-\Delta E/kT)$ , a random number  $\zeta$  is generated uniformly between 0 and 1. The random number is compared with  $\exp(-\Delta E/kT)$ . If it is less than  $\exp(-\Delta E/kT)$  the move is accepted, the next procedure is performed by returning to step 3. If it is more than  $\exp(-\Delta E/kT)$  the move is rejected, return to its old position. Then, having attempted to move a particle again by repeating step 3.

#### 4.5 Radial Distribution Functions and Integration Numbers

The most common way to analyze the structure of solution is to employ the radial distribution function,  $g(r)$ , and the corresponding-running integration number,  $n(r)$ , around various atoms. The radial distribution gives information about the configurationally averaged deviation of the local environment of particle from the values characteristic for the bulk. This function for the  $N$  particles system in configuration  $v$  is obtained with  $r_{ij}$  as

$$g(r) = \frac{N(r)}{\rho 4\pi r^2 dr} \quad (4.9)$$

where  $N(r)$  is the average number of particles in the spherical shell of width  $dr$  at the radial distance  $r$  from the central particle.  $\rho$  is the number density of the system of the pair of the particle in the cubic volume  $V$ . Based on the radial distribution function, solvation shells can be derived from the peaks pronounced over the standard level, and the first solvation number is obtained by the integration of the function up to the first minimum.

The average number of particles within a sphere of a given radius can be determined by

$$n(r) = \rho \int_0^{r_m} g(r) 4\pi r^2 dr \quad (4.10)$$

where  $r_m$  is often chosen as the radial value of the first or second minimum in  $g(r)$ .