



CHAPTER IV

MONTE CARLO METHOD

The " Monte Carlo method " is a computer experiment on a system with many degrees of freedom. Its name is related to the use of " random numbers " to simulate statistical fluctuations in order to generate probability distributions.

A common goal of all " Monte Carlo " computer simulations is to study the microscopic properties of the solutions, such as structural and energetical properties, based on the knowledge of pair potential functions ; 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 energetical informations are very difficult to obtain from spectroscopic measurements in dilute solutions.

In this chapter , the general Monte Carlo method and the Metropolis scheme will be presented together with some important characteristics of the simulation.

4.1 General Monte Carlo Method

Monte Carlo calculations are based on potential functions implementing three assumptions: i) only two body forces are considered, ii) the potential field of the atoms is assumed spherically symmetric and iii) linear additivity is given , i.e. the total configuration

energy, $E(v)$, of the system is written as a sum of pairwise interaction energies between the individual particles $E_{ij}(v)$ of the system.

$$E(v) = \sum_{i < j} E_{ij}(v) \quad (4.1)$$

where v is a configurational coordinate of the particles in a system.

In order to calculate the properties of the system, a canonical ensemble with N particles in a volume V at a constant temperature T must be considered, and to eliminate surface effects periodic boundary conditions are required. The average of any quantity of interest $\langle F \rangle$ can be written as

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

where dv is 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 $\exp(-E(v)/KT)$, shown in eq.(4.2). This is the main 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 (3). In this method, the N configurations are not randomly generated but they are chosen with a probability, $P(\nu)$, and they are evenly weighted with $P(\nu)$. After taking a quite large number of space point M , then eq.(4.2) could be approximated by the sum

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

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

$$P(\nu) = \exp(-E(\nu)/KT) \quad (4.4)$$

Then eq.(4.3) could be reduced to a simple form of

$$\bar{F} = 1/M \sum_{i=1}^M F_i \quad (4.5)$$

where i is the value of the property F of the system after the i^{th} move is carried out, according to the calculating procedures outlined in the following

4.3 Calculating Procedures

Consider a system with N particles in a basic cube of side length L with infinite cube periodicity. The calculating

procedures that should be carried out are the followings:

- 4.3.1 Select initial N configurations according to random numbers generated by a computer.
- 4.3.2 Compute the interaction energy (E) according to eq.(4.1).
- 4.3.3 Perform a random displacement of one particle to a new position, such as particle i from $r_i(x_i, y_i, z_i)$ to $r_i(x_i + \delta_x, y_i + \delta_y, z_i + \delta_z)$, where $\delta_x, \delta_y, \delta_z$ are the maximal allowed displacements. This maximal displacement must be chosen with some cares ; if it is too large , most of the moves will be forbidden, if too small, the 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 i will be returned to its original position, and repeat this step.
- 4.3.4 Compute the new configuration energy (E') according to eq.(4.1) and the change in potential energy (ΔE) from the starting position to the new displaced position , or $\Delta E = E' - E$
- 4.3.5 If $\Delta E < 0$, the displacement would bring the system to a state of lower energy, the displacement to the new configuration is allowed, generate the new displacement according to 4.3.3.
- 4.3.6 If $\Delta E > 0$, compute $\exp(-\Delta E/KT)$, where K is the Boltzmann constant and T is the temperature in Kelvin
- 4.3.7 If $\exp(-\Delta E/KT) < \text{random number}, (l)$, where $0 \leq l \leq 1$ return particle i to its old position $r_i(x_i, y_i, z_i)$. Then, return to step 4.3.3
- 4.3.8 If $\exp(-\Delta E/KT) > l$, the move is allowed , generate the new displacement according to step 4.3.3.

The procedures of calculations are diagrammatically presented in figure 4.1

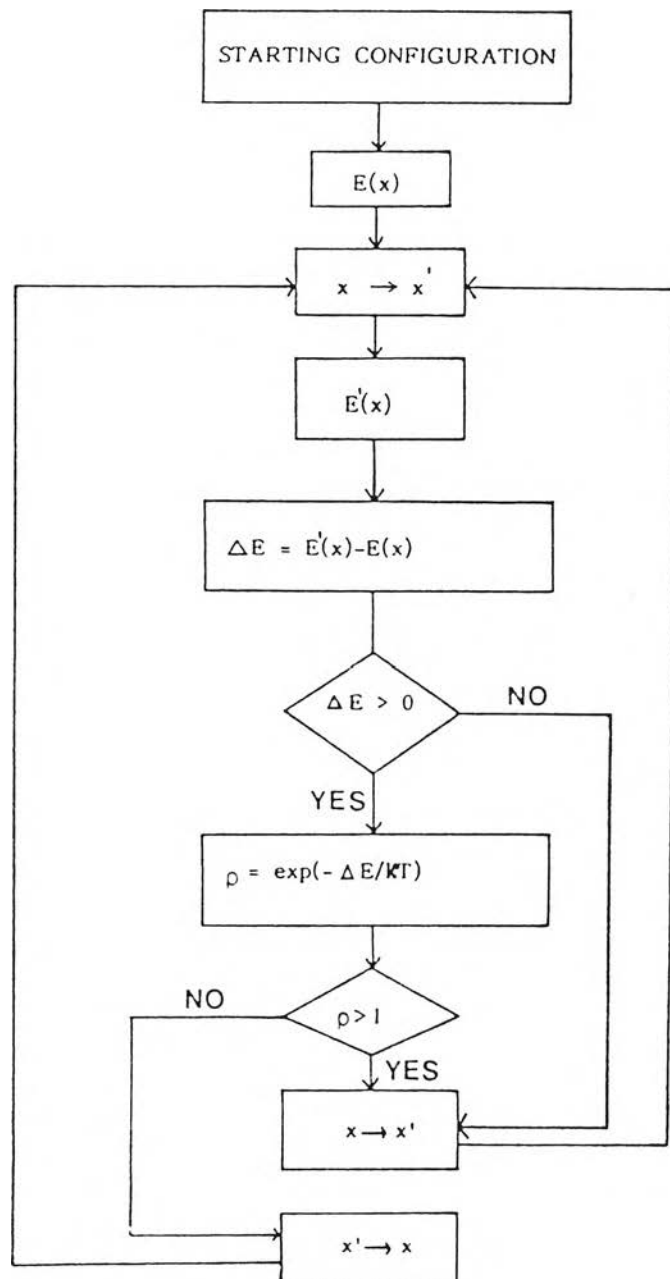


Figure 4.1 Diagram of Monte Carlo calculating procedures.

4.4 Characteristics of the Simulation

4.4.1 Periodic Boundary Condition

In the simulation, the "infinite" system is usually simulated by the use 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, as illustrated in the two dimensional picture in figure 4.2. The surrounding cubes are designated as "replicas" and particles inside each replica are called "ghosts" of the constant set. Each cube contains N (usually some hundreds) particles. By the move of a particle as described above, a particle might be moved to a position outside the basic cube, but within the periodic boundary condition, it only means that the ghost will enter the cube from the opposite side. Therefore, the density inside the basic cube is maintained throughout the simulation. If a small number of particles were confined in an isolated finite cube to the surface of the cube, the proportion of the surface compared to particles inside would be much higher than in any 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.

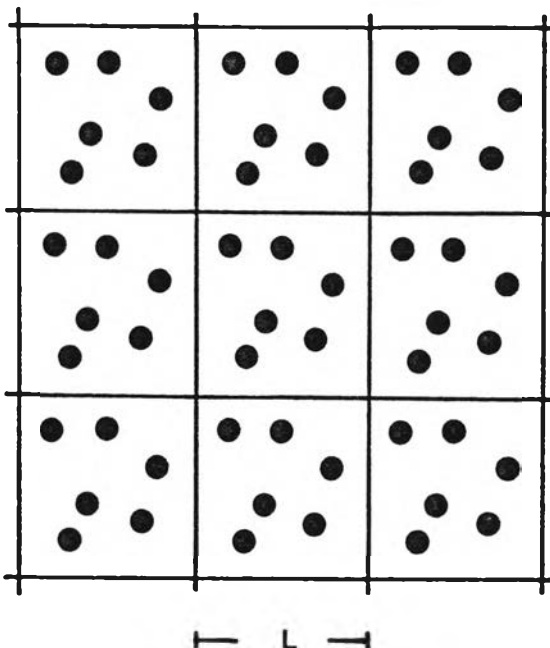


Figure 4.2 Two dimensional illustration of periodic boundary condition

4.4.2 Spherical Cut-off

To obtain the correct energy of the system, assumed to be a summation of pairwise interactions within the basic cube, some further approximations are made.

The first approximation is based on the assumption that contributions to the potential energy from particles beyond a certain distance are insignificant. That means, the potential is truncated after a certain distance. Usually a spherical cut-off is introduced in order to achieve a symmetrical contribution from the surrounding particles, and half of the sidelength of the basic cube is normally used to be the cut-off radius of the sphere.

The second approximation is usually referred as "Ewald method" (75). The interaction with the particles outside the basic cube is also included. This method would probably be generally used, if it did not imply extremely time consuming summations in the simulation.

4.4.3 Radial Distribution Functions and Their Integration

The most common way to analyze the structure of solution is to employ radial distribution functions ($g(r)$) 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 particle system in configuration R_N is obtained with $r = |r_i - r_j|$ as :

$$g(r) = \frac{N(r)}{\rho 4\pi r^2 dr} \quad (4.6)$$

where $N(r)$ is the average number of particles in the spherical shell of width Δr at a radial distance r from the central particle. Based

on the radial distribution functions , 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 K within a sphere of a given radius can be determined by :

$$\bar{n}(r) = \rho \int_0^{r_m} g(r) 4\pi r^2 dr \quad (4.7)$$

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