CHAPTER III

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 numbers in the calculations, was coined by Metropolis in 1947 and used in the title of a paper describing the early work [19].

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

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

3.1 General Monte Carlo Method

Monte Carlo calculations are based on pair potential functions, implementing the assumption that only two body forces are considered, i.e. the total configurational energy, $E(\nu)$, of the system can be written thus as a sum of pairwise interaction energies between the individual particles $E_{ij}(\nu)$ of the system,

$$E(\nu) = \sum_{i<j}\sum E_{ij}(\nu) \qquad (3.1)$$

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

The average of any quantity of interest $\langle F \rangle$ of the system, consisted of N particles in a volume V at a constant temperature T, can be written as

$$\langle F \rangle = \frac{\int \ldots \int F(\nu) \ \exp(-E(\nu)/kT) \ d\nu}{\int \ldots \int \exp(-E(\nu)/kT) \ d\nu} \tag{3.2}$$

where dv is a volume element in three dimensional phase space and k denotes Boltzman constant. If the starting configuration is generated randomly in three dimensional space, integration over many orders of magnitude would be needed for the integral exp(-E(v)/kT) , shown in eq.(3.2). This is the main principle of the general Monte Carlo method, which is however, not practicable.

3.2 Metropolis Monte Carlo Method

The Monte Carlo method introduced by Metropolis et al. [19] is a sampling algorithm based on the idea of " *importance sampling* ". A finite number M of possible configurations are not generated randomly but they are chosen according to a probability P(v). Then eq.(3.2) will be approximated [27] by the sum

$$\langle F \rangle \cong \bar{F} = \frac{\sum_{i=1}^{M} F(\nu) \ P(\nu) \ \exp(-E(\nu)/kT)}{\sum_{i=1}^{M} P(\nu) \ \exp(-E(\nu)/kT)} \tag{3.3}$$

The simplest and most natural possibility of the "*Metropolis Monte Carlo method*" is to choose a specific value of P(v) as a Boltzmann factor

$$P(v) = \exp(-E(v)/kT) \tag{3.4}$$

Then eq.(3.3) can be reduced to a simple form of

$$\overline{F} = \frac{1}{M} \sum_{i=1}^{M} F_i \tag{3.5}$$

where F_i is the value of the property F of the system after the ith configurational change according to the following method.

The initial configuration of N particles in a volume V is generated radomly or taken from a lattice structure of the system. Then a new configuration is obtained by performing a random displacement of one of the particles. The configurational energy according to eq.(3.1) for both the new (E'(v)) and the old (E(v)) systems are calculated and compared. If $\Delta E = [E'(v)) - (E(v)] \leq 0$, the move would bring the system to a state of lower energy. In that case we allow the move and put the particle to this new position. If $\Delta E > 0$, the move will be allowed with the probability $\exp(-\Delta E/kT)$ i.e., a random number $\mathit{1}$ between 0 and 1 will be taken and if $\exp(-\Delta E/kT) \geq \mathit{1}$, the particle will be moved to the new position, if $\exp(-\Delta E/kT) < \mathit{1}$, the old configuration is retained (see Fig.3.1).

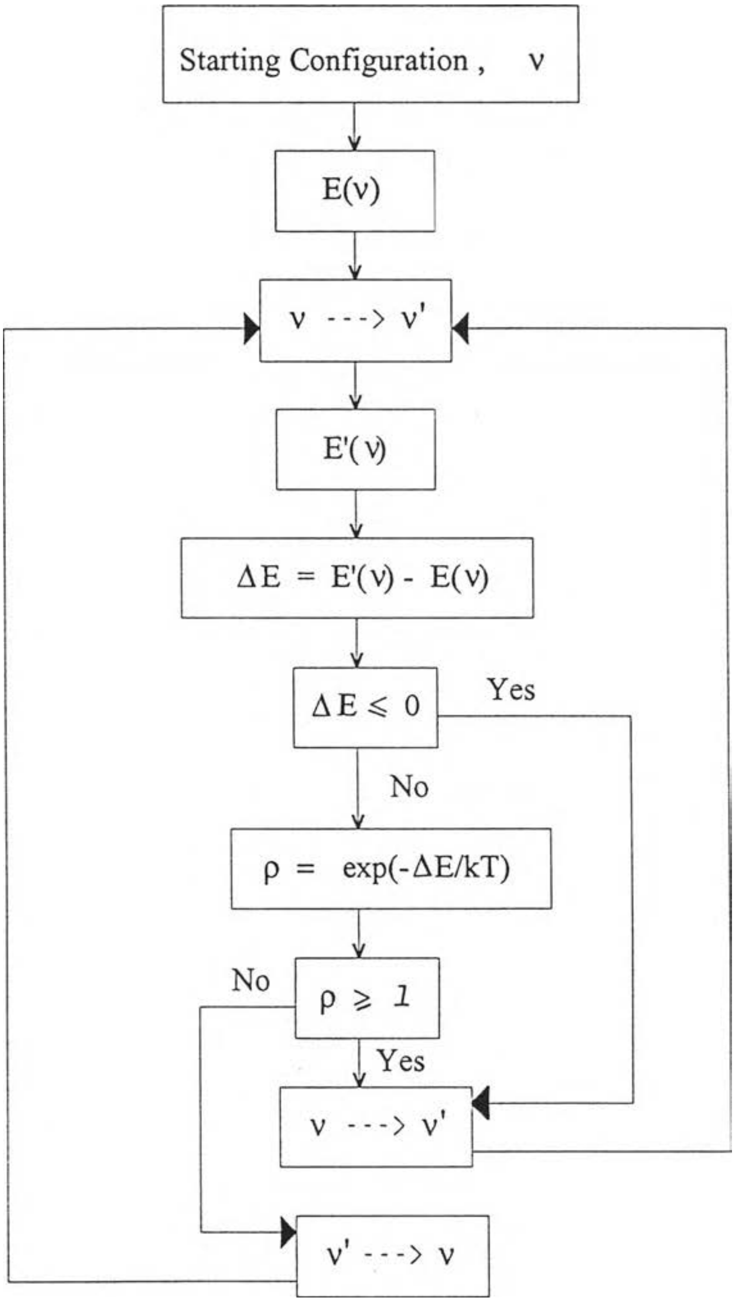

Figure 3.1 The calculating steps of Monte Carlo simulations.

3.3 Characteristic of the Monte Carlo Simulations

3.3.1 Periodic Boundary Conditions

The problem of surface effects can be overcome by implementing periodic boundary conditions. The cubic box is replicated throughout space to form an infinite lattice. 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. A two-dimentional version of such a periodic system is shown in Fig.3.2. The duplicate boxes are labelled A, B, C, etc. As particle **1** moves through a boundary, its images, $\mathbf{1}_A$, $\mathbf{1}_B$, 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.

A side length of the cubic box, L, can be calculated as

$$L = \sqrt[3]{\frac{\sum_{i=1}^{m} N_P M_P}{0.602 D}} \qquad (3.6)$$

where m is the number of species certained in the system,
N_p is the number of particle of species P,
M_p is the ionic or atomic weight of species P, and
D is the experimental density of solution at temperature T and pressure P.

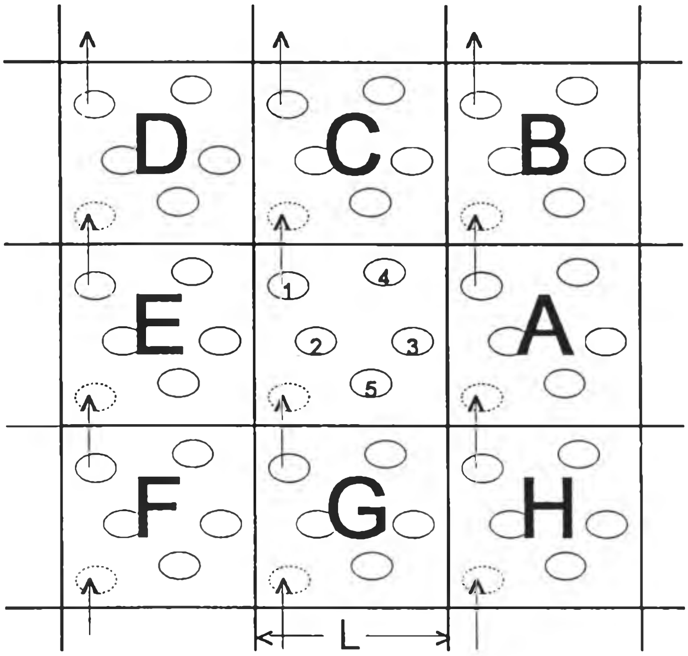

Figure 3.2 A two-dimensional periodic system.

3.3.2 Minimal Image Convention

The heart of Monte Carlo programs involves the calculation of the potential energy of a particular configuration. To calculate the potential energy involving molecule **1** , one assumes pairwise additivity. The interactions between molecule **1** and every other molecules **i** in the simulation box must be included. There are N-1 terms in this sum. However, in principle the interactions between **1** and images $\mathbf{i}_A$, $\mathbf{i}_B$, 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 practicle. For a short-range potential energy function, an approximation may be used to restrict this summation. Consider molecule **1**, lying at the center of a region which has the same size and shape as the basic simulation box (Fig.3.3), it interacts with all the molecules whose centers located 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 Fig.3.3, molecule **1** interacts with molecules **2**, 3_E, 4_E and 5_C . This technique, which is a natural consequence of the periodic boundary condition, was first used in simulations by Metropolis et al.

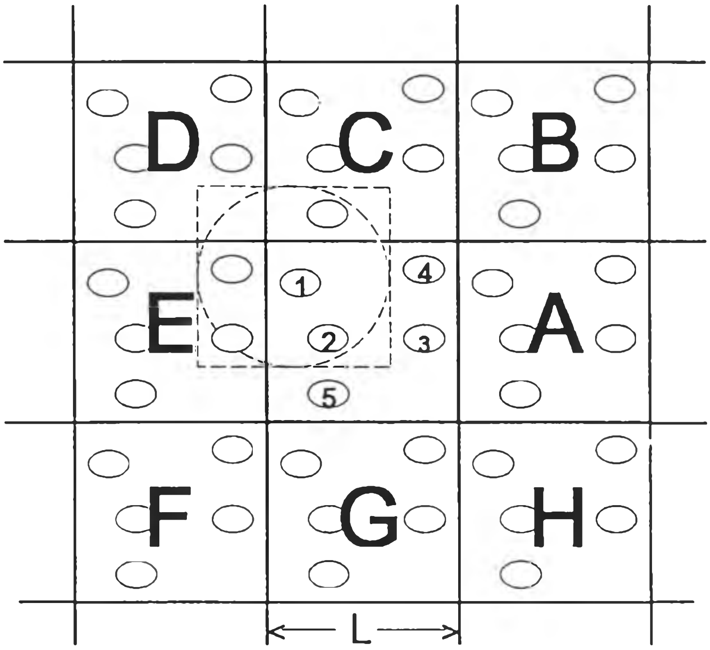

Figure 3.3 The minimal image convention in a two-dimensional system.

3.3.3 Spherical Cut-off

In the minimal image convention, the calculation of the potential energy due to pairwise-additive interactions of N particles involves ½ N(N-1) terms. 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 cutoff can be applied. This means that the pair potential $V(r)$ is set to zero for $r \geq r_C$, where r_C is the cutoff. distance. The dashed circle in Fig.3.3 represents this cutoff, and in this case molecules **2**, $\mathbf{5_C}$ and $\mathbf{4_E}$ contribute to the interaction with **1** , since their centers lie inside the cutoff, whereas molecule $\mathbf{3_E}$ 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 cutoff could be a perturbation, and the cutoff distance should be sufficiently large to ensure that this perturbation is very small.

The cutoff distance must be no greater than ½ L 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.

3.4 Radial Distribution Function (RDF) and its Integration

The radial distribution function gives information concerning the configurationally averaged deviation of the local environment of a particle from the value characteristic of bulk density. This function can be calculated as :

$$g(r) = \frac{N(r)}{\rho 4 \pi r^2 \, dr} \tag{3.7}$$

where N(r) is the average number of particles in a spherical shell of width dr at a radial distance r from the central particle, and ρ is the number density of the pair of the particles in the cubic volume V.

The average number of particles $\overline{K}$ within a sphere of a given radius can be determined by :

$$\overline{K} = \rho_b \int g(r) \, 4\pi r^2 \, dr \tag{3.8}$$

where ρ_b is the number density of one kind of the particle containing in the cubic volume V. For example, the number density of the particle b around the particle a can be determined by :

$$\rho_b = \frac{\text{number of the particle b}}{V} \tag{3.9}$$