CHAPTER III
MONTE CARLO METHOD

The Monte Carlo method was developed by von Newmann, 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 little of a paper describing the early work at Los Alamos (3)

The Monte Carlo techniques are widely used to evaluate numerically, by means of random sampling multidimensional integrals which are too difficult to solve with analytical methods, These methods can be applied also to study properties of condensed matters where the thermodynamical averages obtained over probability distributions are interesting.

Monte Carlo computer simulation as a technique now used in virtually all liquid state work. The Monte Carlo simulations aim to study the microscopic properties of the solutions, such as the structural and energetical properties, based on the knowledge of potential functions. To study liquid behaviour, for instance, how a solute is solvated by solvent molecules in the solution. Spectroscopic techniques are quite difficult to present the structural and energetical information in such dilute solutions.

Basis Principles of Monte Carlo Method

The basis of Monte Carlo computer simulation for fluids is a method first proposed by Metropolis. The principle 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 $E(\nu)$ of the system can be written thus as a sum of pairwise interaction energies between the individual particles $Eij(\nu)$ of the system

$$E(\upsilon) = \sum_{i>j} E_{ij}(\upsilon) \qquad (3.1)$$

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

Average properties of an N-particles system determine under canonical ensemble conditions with volume V at a constant temperature T. The average of any quantity of interest $<F>$ can be written as

$$<F> \quad = \quad \frac{\int ... \int F(v)\exp(-E(v)/kT)dv}{\int ... \int \exp(-E(v)/kT)dv} \qquad (3.2)$$

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

Conditions of Calculations

3.1 Metropolis Monte Carlo Method

The above principle was modified by Metropolis et al. in 1953 (3) based on the idea of importance sampling. In this method, the N configurations are not randomly generated by they are chosen according to a probability, $P(v)$ and they are evenly weighted with $P(v)$. After taking a quite large number of space points M. eq.(3.2), can be approximated by the sum

$$< F > \quad \cong \quad F \quad = \quad \frac{\sum_{i=1}^{M} F(v) P(v)^{-1} \exp(-E(v)/kT)}{\sum_{i=1}^{M} P(v)^{-1} \exp(-E(v)/kT)} \tag{3.3}$$

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

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

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

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

where F_i denotes the value of the property F of the system after the ith configurational change.

3.2 Defining the cube size

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 holds N_P particles for m species, can be calculated as

$$L^3 = \frac{\sum_{p=1}^{m} N_P M_P}{0.602\,D} \qquad (3.6)$$

where D denotes the experimental density of the solution in g/cm^3 at the temperature and pressure which the simulations have been considered; Mp is the ionic or atomic weight of species P

3.3 The Amount of Particles for Simulation

The amount of particles have been investigated in the system is limited by the computer efficiency. The result will be more accurate whenever an increasing number of particles are performed. Anyway, the CPU time has to be considered as well as accuracy. The systems have been found which consist of about 200 particles for the most suitable condition.

3.4 The starting configuration

The starting configuration in the Monte Carlo simulation of all particles has often been generated randomly. However, the particles should be throughout the cube so that the system will be equilibrated very fast. Therefore, the shortest distance between particles l_{min} can be calculated by

$$l_{min} \quad = \quad \sqrt[3]{\frac{L^3}{N}} \tag{3.7}$$

If the simulations are long enough, the random generation is more often used.

3.5 Periodic Boundary Condition

An idea of the computer simulation is to enhance the ability of small systems to simulate the behavior of large systems. This technique considers a certain basis region, usually a cube contains a certain number, N, of molecules. Then imagines that all space is filled by periodic images of this basic unit. In this way, one can consider configurations of an infinite (which must of course be periodic) while only considering a limited number of molecules, N. The problem of surface effects can be also overcome.

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-dimension version of such a periodic system is show in figure 3.1. 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. It is sometimes useful to picture the basic simulation box (in the two dimensional example) as being rolled up to form the surface of a three-dimension torus or doughnut, when there is no need to consider an infinite number of replicas of the system nor any image particles. This correctly represents the topology of the system, if not the geometry. A similar analogy exist for a three-dimensional periodic system.
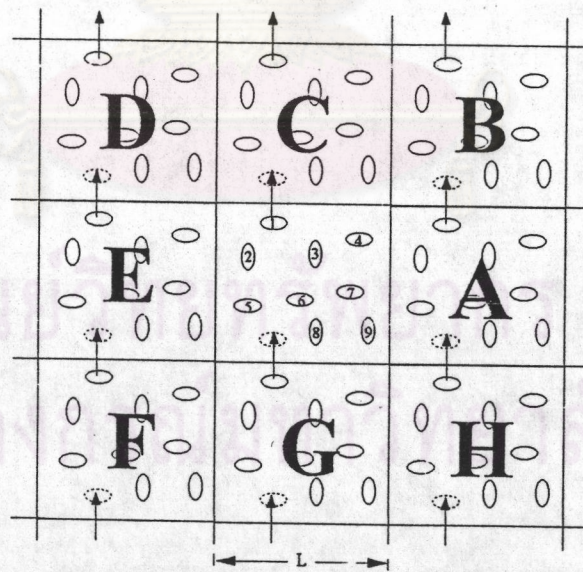

Figure 3.1 A two-dimensional periodic.

3.6 Minimal Image Convention

The heart of Monte Carlo programs involves the calculation of the potential energy of a particular configuration. To calculate contributions to the potential energy involving molecule 1, one assume pairwise 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. However, in principle the interactions between molecule 1 and images i_A, i_B, etc. lying in the surrounding boxes must be included as well. This is an in finite number of terms, and of course it is impossible to calculate in practice. For a short-range potential energy function, and 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 3.2, molecule 1 interacts with molecules 2 , 3 and 8_C. This technique, which is a natural consequence of the periodic boundary condition, was first used in simulations by Metropolis et al (3).

3.7 The spherical cut-off

In the minimal image convention, the calculation of the potential energy due to pairwise-additive interactions involves $\frac{1}{2}N(N-1)$ 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 cutoff can be applied. This means setting the pair potential $\upsilon(r_{ij})$ to zero for $r_{ij} \geq r_c$, where r_c is the cutoff

distance. The dashed circle in figure 3.2 represents this cutoff, and in this case molecules 2, 3 and 8_C contribute to the interaction with 1, since their centers lie inside the cutoff, whereas molecule 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 cut-off 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 ½L 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.
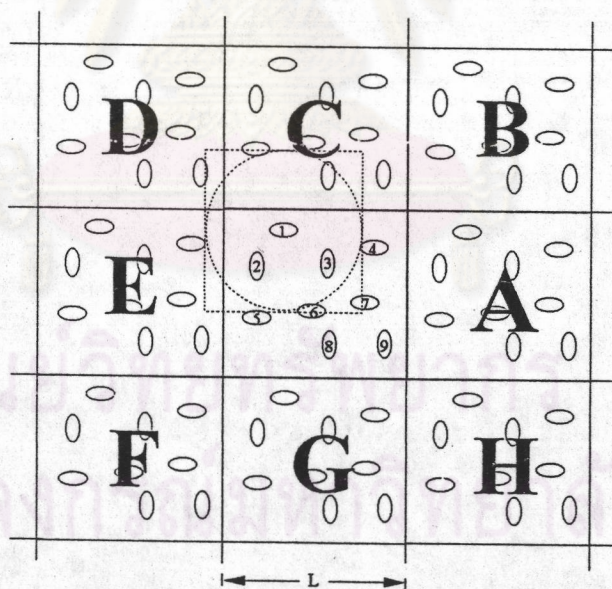

Figure 3.2 The minimum image convention in a two-dimensional system.

3.8 The 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 the dimensionality of the system. In another meaning, long-range interaction is one in which all the particles lying outside the cutoff 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* (22) and *the reaction field method* (23) 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 images. the reaction field method introduced without the assumption of the periodicity is to treat all molecules beyond the cutoff sphere of radius from a center as forming a continuum with a given dielectric constant; therefore, any charge lying inside the cutoff sphere will polarize the continuum and create a reaction field at the center.

The Ewald sum

The Ewald sum procedure is the oldest one which is perfectly consistent with periodic boundary conditions. This procedure is a technique for efficiently summing the interaction between a particle and all its periodic images. Due to the periodic conditions, the potential energy per particle for a system interacting through a central force type potential is given by

$$V = \frac{1}{N} \sum_n \sum_{j<i} \phi(r_{ij}+L_n) \qquad (3.8)$$

where the summations is to be taken over all the molecular pairs (i,j) within the simulation box, and the cell vectors **n** extend to the infinite lattice.

In this technique the summation in equation (3.8) is actually attempted by thinking every charge as made up of a Gaussian distribution. The summation is then split into two parts : One from the tail of a Gaussian distribution, the other from the rest. The former results in the complementary error function erfc(x), whereas the latter is carried out in the reciprocal lattice space (Fourier **k** space).

For charge-charge interactions, the resulting formula is

$$NV = \sum_n \sum_{i \le j} \frac{\text{erfc}(a|r_{ij}+L_n|)}{|r_{ij}+L_n|} + \frac{1}{\pi V} \sum_{k \ne 0} \sum_{i \le j} |k|^{-2} e^{(-\pi^2/a^2 k^2)} \cos(2\pi k - r) \qquad (3.9)$$

where α is a splitting parameter.

The reaction field method

The reaction field method was introduced without the assumption of the periodicity. The basic physics behind this method is to treat all molecules beyond the cut-off sphere of radius **R** from a center charge q_i as forming a continuum with a given dielectric constant ε_F. Any charge q_i lying inside the cut-off sphere will polarize the continuum and create a reaction field at the center. From electrostatic theory, that reaction field can be shown to be

$$F(r=0)=-\frac{1-\varepsilon_F}{\varepsilon_F-\frac{1}{2}}\frac{q_i r_j}{R^3} \qquad (3.10)$$

where r_j is the position vector of the charge q_j

Steps of Calculations

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 3.3. A summary of procedures which are carried out is the following.

1.) Determine an initial configuration (υ) that is chosen by which the positions of the N particles are generated randomly or from a previous simulation.

2.) The computer then calculates the interaction energy ($E(\upsilon)$) of this configuration according to equation (3.1) based on the potential function.

3.) The computer chooses randomly an integer from 1 to N, the particle which will be determined to move. Then move the labeling particle ($\upsilon \rightarrow \upsilon'$) in succession according to the following prescription :

$$X \rightarrow X + \alpha\xi_1$$
$$Y \rightarrow Y + \alpha\xi_2$$
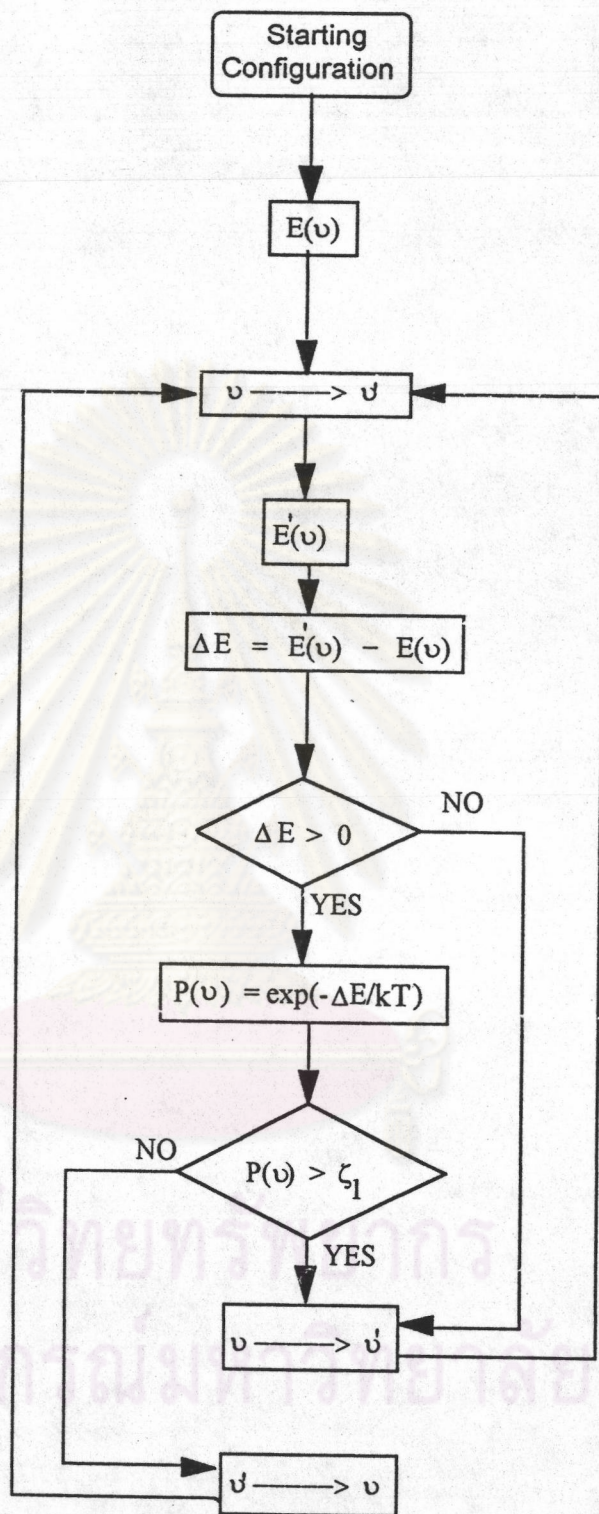$$Z \rightarrow Z + \alpha\xi_3$$

Figure 3.3 The calculating steps of Monte Carlo Simulations.

where a is the maximum allowed displacement, which for the sake of this argument is arbitrary, and ξ_1, ξ_2 and ξ_3 are random numbers between -1 and 1. 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, 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 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 ($E'(\upsilon)$) and the change in different energy ΔE between the new and the old configuration, which is caused by the move.

$$\Delta E = E'(\upsilon) - E(\upsilon) \qquad (3.11)$$

The next step in MC move is to determine ΔE. There are two cases to consider

4.1) If the move is downhill in energy ($\Delta E < 0$), then probability of state υ is greater than state υ' 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 $P(\upsilon)$, can be readily expressed as the Boltzman factor of the energy difference.

$$P(\upsilon) \quad = \quad \exp(-\Delta E/kT) \qquad\qquad (3.12)$$

where k is the Boltzmann constant and T is the temperature in Kelvin.

To accept a move with a probability of $\exp(-\Delta E/kT)$, a random number ξ_4 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.

Radial Distribution Functions and Integration Numbers

The most common way to analyze the structure of solution is to employ the radial distribution functions 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 υ is obtained with r_{ij} as

$$g(r) \quad = \quad \frac{N(r)}{\rho 4\pi r^2 dr} \qquad\qquad (3.13)$$

where N(r) is the average number of particles in the spherical shell of width dr at a radial distance r from the central particle. ρ is the number density of the system of the pair of the particles in the cubic volume V. 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 within a sphere of a given radius can be determined by

$$n(r) = \rho \int_0^{r_m} g(r) 4\pi r^2 dr \tag{3.14}$$

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