

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 at Los Alamos.(24)

A common goal of all 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 structural and energetical informations are very difficult to obtain from spectroscopic measurements in dilute solutions.

In this chapter, the principles of Monte Carlo algorithms (Metropolis, Periodic Boundary Condition, Minimal Image convention, Spherical Cutoff, Long-range Interactions) will be presented together with some review of Monte Carlo simulations of electrolyte solutions.

3.1 Principles of Monte Carlo Method

Classical Monte Carlo calculations 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 can be written thus as a sum of pairwise interaction energies between the individual particles $E_{ij}(v)$ of the system.

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

(3.1)

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

$$\langle F \rangle = \frac{\int \dots \int F(v) \exp(-E(v)/kT) dv}{\int \dots \int \exp(-E(v)/kT) dv} \quad (3.2)$$

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.(3.2). This is the main principle of the general Monte Carlo method, which is however, not practicable.

3.2 Algorithms

3.2.1 Metropolis Monte Carlo Method

The above was modified by Metropolis et al. in 1953 (24). In this method, the N configurations are randomly generated but accepted with respect to their 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

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

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

Boltzmann factor :

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

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

$$\bar{F} = 1 / M \sum_{i=1}^M F_i \quad (3.5)$$

where i is the value of the property F of the system after the i^{th} configuration change.

3.2.2 Periodic Boundary Condition

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-dimensional version of such a periodic system is shown in figure 3.1. The duplicate boxes are labelled 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 the 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-dimensional 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 .

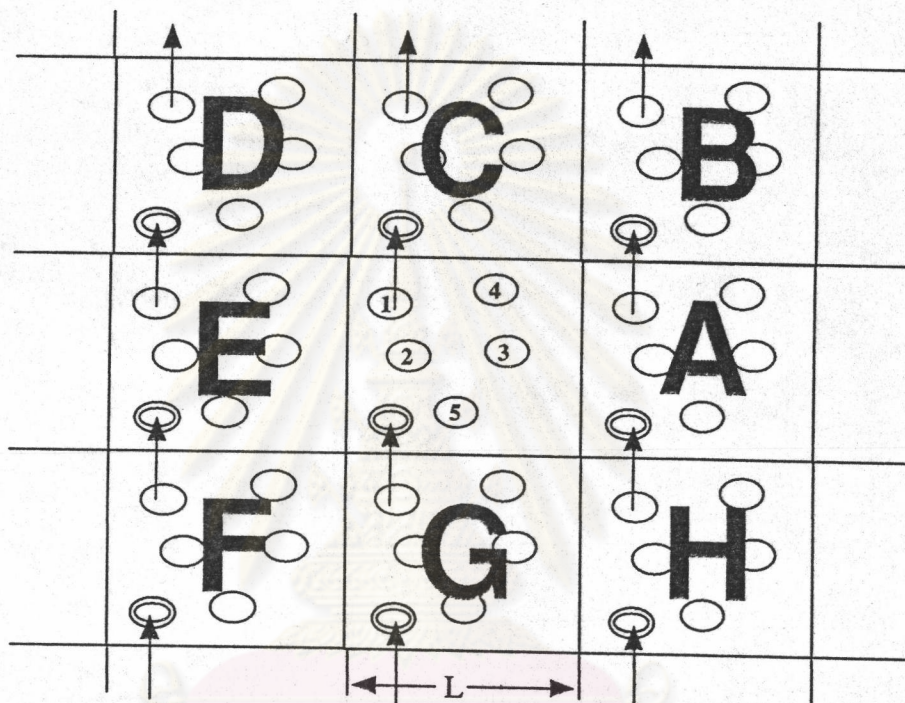


Figure 3.1 : A two-dimensional periodic system.

3.2.3 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 interactions 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 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 centre of a region which has the same size and shape as the basic simulation box (figure 3.2). Molecule 1 interacts with all the molecules whose centres 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_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.

3.2.4 Spherical Cut-off

In the minimal image convention, then, 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 1000 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 $v(r)$ to zero for $r \geq r_c$, where r_c is the cutoff distance. The dashed circle in figure 3.2 represents this cutoff, and in this case molecules 2 and 4_E contribute to the interaction with 1, since their centres lie inside the cutoff, whereas molecules 3_E and 5_C do 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 $\frac{1}{2}L$ for consistency with the

minimal image convention, and it is applicable only to rapidly decreasing potential terms, e.g. $1/r^6$ or exponential terms.

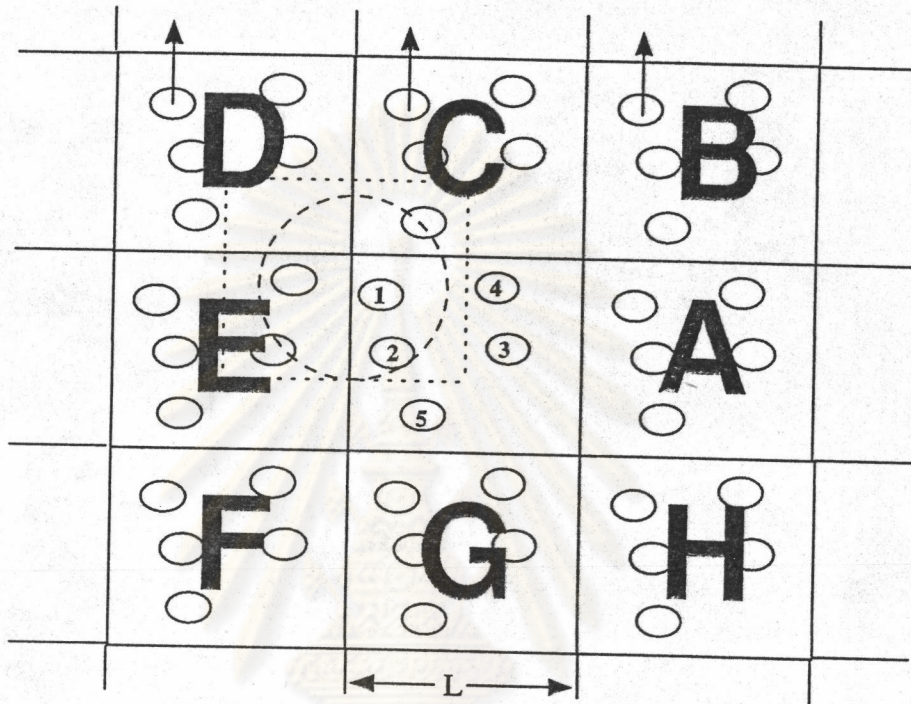


Figure 3.2 : The minimum image convention in a two-dimensional system.

3.2.5 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 interaction. Long-range interactions are a serious problem for the computer simulator, since their range is greater than half the box length. So far, there have been two widely used methods which can be employed to handle the problem of long-range interaction. The two



methods will be shown as following :

The Ewald sum , (25)

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 :

$$V = \frac{1}{N} \sum_{\mathbf{n}} \sum_{j < i} \phi(\mathbf{r}_{ij} + L\mathbf{n}) \quad (3.6)$$

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 (3.6) 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 inteactions, the resulting formula is :

$$NV = \sum_{\mathbf{n}} \sum_{i \leq j} \frac{\text{erfc}(\alpha |\mathbf{r}_{ij} + L\mathbf{n}|)}{|\mathbf{r}_{ij} + L\mathbf{n}|} + \frac{1}{\pi V} \sum_{\mathbf{k} \neq 0} \sum_{i \leq j} |\mathbf{k}|^{-2} e^{(-\pi^2/\alpha^2 \mathbf{k}^2)} \cos(2\pi \mathbf{k} \cdot \mathbf{r}) \quad (3.7)$$

where α is a splitting parameter.

The reaction field method , (26)

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 cutoff sphere of radius R from a center charge q_i as forming a continuum with a given dielectric constant ϵ_F . Any charge q_j lying inside the cutoff sphere will polarize the continuum and create a reaction field at the center. From electrostatic theory, that reaction field can be shown to be

$$F (r = 0) = - \frac{1 - \epsilon_F}{\epsilon_F + \frac{1}{2}} \frac{q_j r_j}{R^3} \quad (3.8)$$

where r_j is the position vector of the charge q_j .

3.3 Calculating Procedures

Consider a system consisting of N particles in a basic cube of side length L with infinite cube periodicity. A summary of procedure are the followings :

First, an initial configuration is chosen by which the positions of the particles are selected randomly or from a previous simulation or a solid state structure. The computer then calculates the potential energy of this configuration from equation (3.1).

Second, the computer chooses at random an integer from 1 to N ; this determines the label of the particle which it will attempt to move. A trial move for this particles is constructed by choosing displacements in the x , y and z directions, each of which may vary randomly from $-\Delta$ to $+\Delta$. If the trial move carried the particle outside the basic cube, it is brought back to the other side according to the boundary condition. The parameter Δ may be chosen on the basis of previous experience so as to improve the quality of the results, or in order to guarantee a desired acceptance rate.

Third, the computer decides whether to accept the trial move. This is done on

the basis of a specified set of transition probabilities which depend on the energy difference ΔE between the new and old configuration divided by kT , ($\Delta E/kT$). In the common way, the trial move always accepted if it lowers the energy. The trial move is accepted with probability respect to the $\exp(-\Delta E/kT)$ if it raises the energy by ΔE . If the move is rejected, the old configuration is counted as having occurred again in the computation averages.

3.4 Review of Monte Carlo Simulation of Electrolyte Solutions

Numerous studies based on Monte Carlo simulations for solutions have already been published. Most of such studies have concerned about electrolyte or aqueous solutions due to their significant roles in solution chemistry and biochemical processes. The discussions were mostly based on the structural properties concerning the first hydration shell structure and how solute molecules (water molecules) arrange themselves around the metal ion. In 1976, a water-water potential function (27) has been constructed by , O. Matsuoka, E. Clementi and M. Yoshimine (known as MCY potential function), which rapidly raised the studies of aqueous solution using Monte Carlo. In the early stage, the studies on metal ion in water concerned mostly about monovalent metal ions such as Li^+ , Na^+ , K^+ (28-30) and included some divalent metal ions such as Mg^{2+} , Ca^{2+} (31,32) . Almost every studies on the simple monovalent and divalent metal ions assumed pairwise additive of potential functions, and they gave results in agreement with experimental data. But some problems occurred when such studies were performed on aqueous solutions of some divalent or transition metal ions as Be^{2+} (33), Ni^{2+} (34), Fe^{2+} (35) and Cu^{2+} (36,37) . Assuming pairwise additive interaction only was not enough to describe correctly the structure of the hydrated metal ions, thus the at least 3-body terms (non-additive term) had to be included in the potential functions to improve the quality of the simulations. Among the N-body terms, the first, i.e. the three-body terms were the most widely used in simulations , whereas the other terms was rarely used due to the enormous computer effort needed for the construction of such potential function and in the simulation.