

CHAPTER III

THE MONTE CARLO METHOD

Monte Carlo techniques have attracted significant attention because they are suitable for optimization problems of a very large scale. One such method, known as simulated annealing, it has effectively "solved" the famous *traveling salesman problem* of finding the shortest cyclical itinerary for a traveling salesman who must visit each of N cities in turn. Amazingly, the implementation of the algorithm is quite simple. This is an example of *combinatorial minimization*. There is an objective function to be minimized, as usual, but the space over which that function varies is not simply the N -dimensional space of N continuously variable parameters. Rather, it is a discrete, but very large, configuration space, like the set of possible sequences of cities. The number of elements in the configuration space is factorially large, so that they cannot be explored exhaustively. Further more, since the set is discrete, we are deprived of any notion of *continuing downhill in a favorable direction*. The concept of *direction* may not have any meaning in the configuration space.

Monte Carlo techniques are generally used to evaluate numerically, by means of random sampling, multidimensional integrals which are too difficult to solve with analytical methods. These methods can also be applied to study properties of condensed matter, where the thermodynamical averages obtained over probability distributions are of interest and a common goal is to study the microscopic properties of the substance, such as the structural and energetic properties, based on a knowledge of the potential functions, *e.g.*, how a solute influences the solvent structure or how a solute is solvated by solvent molecules in the solution. Such structural and energetic information is very difficult to obtain experimentally (*e.g.*, by spectroscopic measurements) because of the structures' instability, or a high degree of dilution.

3.1 Basic Principles of the Monte Carlo Method

Monte Carlo calculations are based on pair potential functions. The simplest way to use such functions is under the assumption of linear additivity, i.e., the total configurational energy $E(v)$ of the system can be written as a sum of pairwise interaction energies between the individual particles $E_{ij}(v)$ of the systems,

$$E(v) = \sum_{i>j} E_{ij}(v) \quad [3.1],$$

where v represent the configurational coordinates of the particles in the 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. 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 the multi-dimensional configuration space and K denotes Boltzmann constant. If the starting configuration is generated randomly in three dimensional space, integration over many orders of magnitude of $\exp(-E(v)/KT)$ is needed. This is the main principle of the crude Monte Carlo method, which, however, is not practicable.

The above algorithm was modified by Metropolis *et al.* (1) based on the idea of *importance sampling*. A finite number M of possible configurations are not generated randomly, but they are chosen and weighted according to a probability $P(v)$. After sampling a large number of space points M , Eq. [3.2] can be approximated by the sum

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

The simplest and most natural possibility is the *Metropolis Monte Carlo method*, in which $P(v)$ is chosen to be a Boltzmann factor,

$$P(v) = \exp(-\Delta E(v)/KT) \quad [3.4].$$

Then Eq. [3.3] will be reduced to a simple summation of the type

$$F = \frac{1}{M} \sum_{i=1}^M F_i \quad [3.5],$$

where F_i is the value of the property F of the system after the i th configurational changes and M is a large number of space points.

3.2 Conditions for the Calculations

To perform the Monte Carlo simulations, the following conditions are necessarily required, and have to be properly satisfied.

3.2.1 *The cube size*

A cubic box has been often used for holding all investigated particles. The length of the cube side, $L(\text{\AA})$, for m species, and N_p particles with the atomic/molecular weight of M_p for each species p , is calculated by

$$L^3 = \frac{\sum_{p=1}^m N_p M_p}{0.602D} \quad [3.6],$$

where D is the experimental density of the solution, in g/cm^3 , at the temperature and pressure which the simulations take place.

3.2.2 *The constant number of particle*

The number of particles in the investigated system depends on the computer efficiency. The simulation results will be more accurate whenever

number of particles is increased. In addition, the CPU time has to be also considered. It has been found that about 200 particles provide the best compromise between accuracy and time cost.

3.2.3 *The starting configuration*

In the first step of the MC simulations, the starting coordinates of all particles (atoms/molecules) have to be generated either randomly or as a crystal lattice of the identical system. However, it is important that at the starting configuration, particles should be distributed homogeneously. Therefore, the shortest distance between particles, l_{\min} can be estimated by

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

If the simulations are long enough, differences between the results obtained from different starting configurations are found to be negligible. However, the random one is more often used.

3.2.4 *The periodic boundary condition*

A key idea of this method is to enhance the ability of small systems to simulate the behavior of large systems. This technique considers a certain basic region, usually a cube, containing a certain number N of molecules. Then one imagines that all space is filled by periodic images of this basic unit. In this way, one can consider configurations of an infinite system (which must of course be periodic) while only considering a limited number N of molecules. The great advantage is to avoid *surface effects*, which can make the particles situated near to the surface less solvated than the rest, which would otherwise be very large for small N . Often one uses the *nearest image distance convention* according to which a given molecule i is supposed to interact only with the periodic image of another molecule j which lies closest to i . In fact, if the range of the molecule distances is less than half the edge of the cube, it is convenient to force this by truncating the potential.

According to the periodic boundary condition, 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 neighboring 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 which box the image lies in) 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-dimensional torus or doughnut, so 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. A similar analogy exist for a three-dimensional periodic system.

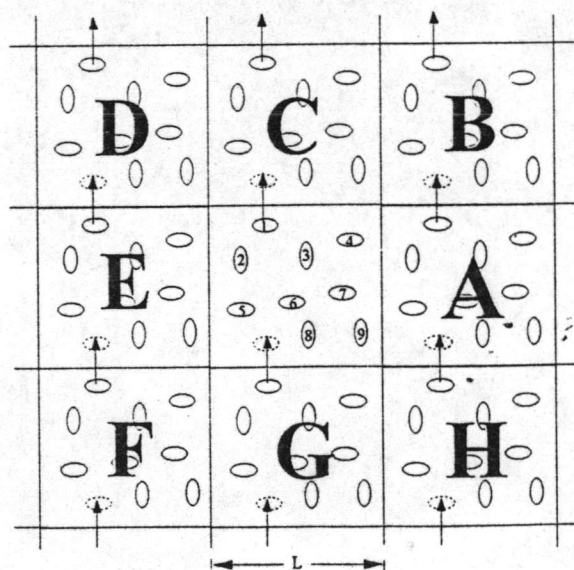


Figure 3.1 A two-dimensional periodic system.

3.2.5 The spherical cutoff

In the minimal image convention, the calculation of the potential energy due to pairwise-additive interactions involves $\frac{1}{2}N(N-1)$ terms where N denotes number of particles in the central box. This may still be a very substantial calculation for a system of, for example, 1,000 particles. Since the largest contribution to the potential comes from interactions with neighbors close to the molecule of interest, known as short-range interactions, a spherical cutoff can be applied. This means setting the pair potential $v(r_{ij})$ 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 contribute to the interaction with 1, since their centres lie inside the cutoff, whereas other molecules do not contribute. In a cubic simulation box of side L , the number of neighbors 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 is 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 $L/2$ 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.

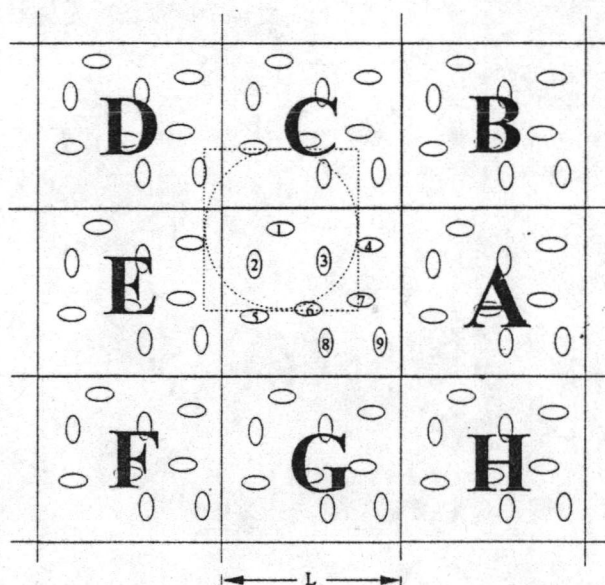


Figure 3.2 The minimum image convention in a two-dimensional system.

3.2.6 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, a long-range interaction is one in which all the particles lying outside the cutoff sphere of a given particle is not taken into consideration. The charge-charge, charge-dipole, dipole-dipole and charge-quadrupole interactions are examples of strong interactions. 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* (42) and *the reaction field method* (43) have been two widely used methods which can be employed to handle the problem of long-range interactions. 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 centre 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 centre.

3.3 Steps of Calculations

Assuming N particles in a given configuration and in a given volume at temperature T , the Monte Carlo algorithm consists essentially of the following steps (Figure 3.3):

1. Place the N particles in any configurations (ν).
2. Calculate the interaction energy, $E(\nu)$, based on the pair potential.
3. Move the system from a state ν to any one of its neighboring states ν' with equal probability. An arbitrary definition of a neighboring state is illustrated in Figure 3.4. This diagram shows six atoms in a state ν ; to construct a neighboring state ν' one atom (i) is chosen randomly and displaced from its position r_i^ν to any random position $r_i^{\nu'}$ inside the square R that would be a small cube. The maximum displacement is an adjustable parameter that governs the size of the region R .

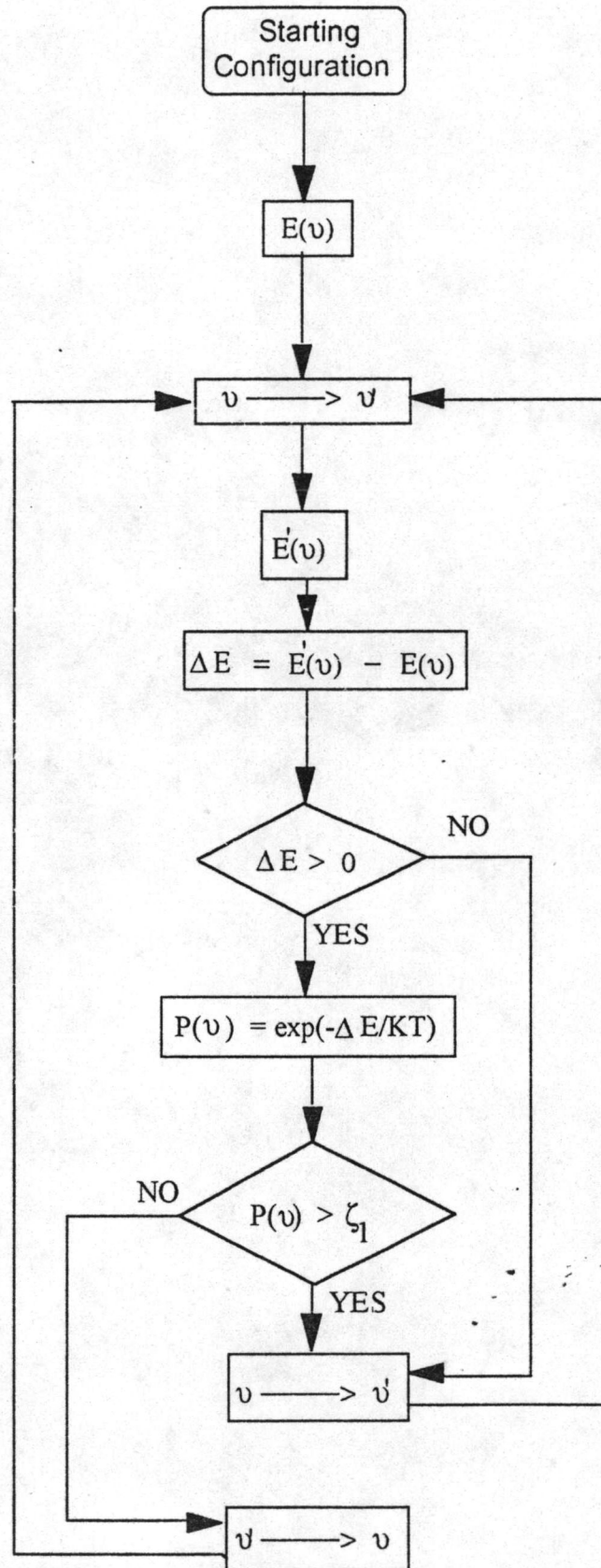


Figure 3.3 The calculating steps of the Monte Carlo simulations.

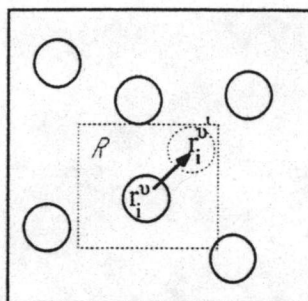


Figure 3.4 State v' is generated from state v by displacing atom i from r_i^v to $r_i^{v'}$.

4. Calculate the new configuration energy, $E'(v)$, and the change in the energy of the system, $\Delta E = E'(v) - E(v)$, which is caused by the move.

The next step in the MC move is to analyze ΔE . Two possibilities have to be considered:

- 5a. If the move is downhill in energy ($\Delta E < 0$), then the 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.
- 5b. If the move is uphill in energy ($\Delta E > 0$), the move is accepted with a probability $P(v)$, where

$$P(v) = \exp(-\Delta E/KT) \quad [3.8],$$

and K is the Boltzmann constant.

To accept the move with the probability of $P(v)$, a random number ζ between 0 and 1 is generated. This random number is, then, compared with $P(v)$. If ζ is less than $P(v)$ the move is accepted. This procedure is illustrated in Figure 3.5.

During the run, suppose that a particular uphill move, ΔE is attempted. If at that point the random number ζ_1 is chosen (see Figure 3.5), the move is accepted. If ζ_2 is chosen the move is rejected.

If the uphill move is rejected, the system remains in state ν in accord, the atom is retained at its old position and the old configuration is recounted as a new state in the chain.

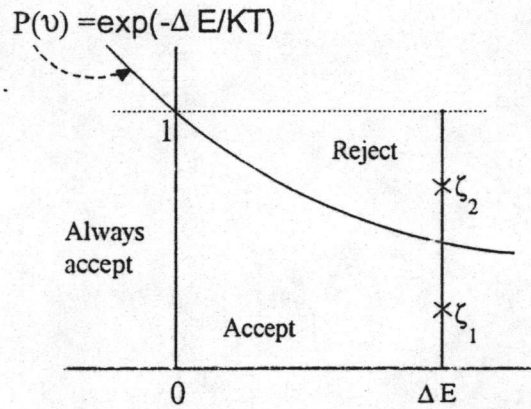


Figure 3.5 Accepting uphill moves in the MC simulation.

3.4 Radial distribution functions and running integration numbers

The most common way to analyze the structure of the solution is to employ the radial distribution functions $g(r)$ and the corresponding running integration number $n(r)$. This function, representing the average distribution of distances between N_y particles of type y and N_x particles of type x can be calculated as:

$$g_{xy}(r) = \frac{N(r)}{\rho 4\pi r^2 dr} \quad [3.9],$$

where $N(r)$ is the average number of particles of the other type in a spherical shell of width dr at a radial distance r from the central particle, and ρ is the number density of the pairs, $N_x N_y / V$, in the cubic volume V .

The average number of particle of type y within a sphere of a given radius r_m from the particle x can be determined by:

$$n(r) = \rho_y \int_0^{r_m} g_{xy}(r) 4\pi r^2 dr \quad [3.10],$$

where r_m is often chosen as the distance up to the first or second minimum of $g_{xy}(r)$ and ρ_y is number density of particle y , N_y/V .