

# The Development and Comparison of Molecular Dynamics Simulation and Monte Carlo Simulation

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**Abstract.** Molecular dynamics is an integrated technology that combines physics, mathematics and chemistry. Molecular dynamics method is a computer simulation experimental method, which is a powerful tool for studying condensed matter system. This technique not only can get the trajectory of the atom, but can also observe the microscopic details of the atomic motion. By studying the numerical integration algorithm in molecular dynamics simulation, we can not only analyze the microstructure, the motion of particles and the image of macroscopic relationship between them and the material, but can also study the relationship between the interaction and the macroscopic properties more conveniently. The Monte Carlo Simulation, similar to the molecular dynamics, is a tool for studying the micro-molecular and particle nature. In this paper, the theoretical background of computer numerical simulation is introduced, and the specific methods of numerical integration are summarized, including Verlet method, Leap-frog method and Velocity Verlet method. At the same time, the method and principle of Monte Carlo Simulation are introduced. Finally, similarities and differences of Monte Carlo Simulation and the molecular dynamics simulation are discussed.

## 1. Introduction

The mean of numerical simulation in the field of engineering and scientific research currently has gradually become one of the most useful solutions for solving some complicated problems. As a useful tool with more commercial and productive natures than the traditional one in scientific researches, the mean of numerical simulation make some expensive, costly, and even dangerous experiments achievable, which meanwhile offers more detailed and complete data by comparing to those that cannot be calculated and observed visually. [1-3]

Currently, there are three units of measurement in computational simulation including microscale (0.1~10nm, 1~10ps), mesoscale (10~1000nm, 10~1000ns), and macroscale (>1 $\mu$ m, >1 $\mu$ s). Basically, microscale is widely applied in numerous researches such as observations of chemical reaction, structural analyses of molecule, and simple studies of kinetic. We mainly use Molecular dynamics [4] and Monte Carlo simulation [5] to gain the possible outcomes because the objects in experiment can be specific enough to the motional details of every atomic or molecule, which offer possible solutions for researches to understand exactly both physical and chemical natures in microcosmic perspective. However, it is difficult to achieve the ideal calculation amounts based on current technology because the cost led by the carefulness of the study may be too costly to afford, especially in the research of studying kinetics feature. Macroscale simulation is primarily applied in the study of rheological theory research and material machining analysis, which includes



ADFE, BEM, FDM and so on. By using the means in the macroscale perspective, we can easily detect every macro features of the entire simulation system. However, we might lose some important fine structures during the process of coarse graining. Mesoscale simulation can be defined as a connection between microscale simulation and macroscale simulation, which includes both MesoDyn and DPD [6]. By using these means, we can largely reduce the calculation amount and simulation time without losing much details. However, this theory is still immature and needs more researches to improve in the future.

## **2. The Molecular Dynamics Simulation**

The so-called molecular dynamics simulation refers to the simulation of the interaction and movement of microscopic particles in the multi-body system consisting of nuclei and electrons, assuming each nucleus moves according to Newton's law under the potential field that contains all other nuclei and electrons, so as to get the system of particles in the trajectory. And then according to the statistical method of physical, to calculate the material structure and properties of macroeconomic performance [7].

### *2.1 The General Process of Molecular Dynamics Simulation*

The first step in molecular dynamics simulation is to determine the initial configuration, and a lower energy initial configuration is the basis for molecular modeling. The general molecular initial configuration is mainly from experimental data or quantum chemistry calculations. The molecular dynamics issues the atomic velocity of the constituent molecules after determining the initial configuration, which is generated randomly according to the Boltzmann distribution. Since the velocity distribution conforms to Boltzmann's statistics, at this stage, the temperature of the system is constant.

The equilibrium phase is formed by the molecules determined by the previous step, and the parameters such as configuration and temperature are monitored when the equilibrium phase is constructed.

After entering the production phase, the molecules in the system and the atoms in the molecule begin to move according to the initial velocity, and it is conceivable that there will be attraction, repelling, and even collision. At this time, the trajectories of each particle are calculated based on the interaction between Newtonian mechanics and the pre-given particle, during which the total energy of the system is constant, yet the internal potential energy and kinetic energy of the molecule are continuously transformed from each other, so that the temperature of the system is also changing. Throughout the process, the system will traverse the various points on the potential energy surface, while the calculated sample is extracted in this process.

The potential energy of the system is calculated by the various states of the sampled system, and the configuration integral is calculated.

## **3. Numerical integration of motion equations**

Using the molecular mechanics force field, it is assumed that any atomic motion in the system conforms to the classical Newtonian mechanical equation. When given the initial coordinate and velocity, the motion trajectories of the atoms are obtained after integration. The basic point of the computer simulation method is to utilize the high-speed and preciseness of modern computer for numerical integration of hundreds or even thousands of molecules of the motion equations. Many different integration methods have been reported, and their efficiency and accuracy are different. Basically, the finite difference method is used to integrate the second order ordinary differential equations. Commonly used methods are: Verlet method, leap-frog method, Velocity Verlet method, Beeman's method, Gear method, and so on.

### *3.1 Verlet method*

The Verlet algorithm proposed by Verlet is the most widely used yet the simplest algorithm in the molecular dynamics [8]. It uses the position of the atom at time and the acceleration and the position of time to calculate the position of time. The location of the particles expanded by Taylor formula is,

$$r(t + \delta t) = r(t) + \frac{d}{dt}r(t)\delta t + \frac{1}{2!}\frac{d^2}{dt^2}r(t)(\delta t)^2 \quad (1)$$

Replace in equation (1) to - can get:

$$r(t - \delta t) = r(t) - \frac{d}{dt}r(t)\delta t + \frac{1}{2!}\frac{d^2}{dt^2}r(t)(\delta t)^2 \quad (2)$$

Equation (1) minus equation (2), then

$$v(t) = \frac{dr}{dt} = \frac{1}{2\delta t}[r(t + \delta t) - r(t - \delta t)] \quad (3)$$

Equation (1) plus equation (2), then we can get:

$$r(t + \delta t) = -r(t - \delta t) + 2r(t) + \frac{d^2}{dt^2}r(t)(\delta t)^2 \quad (4)$$

Since  $\frac{d^2}{dt^2}r(t) = a(t)$ , hence the position at time can be predicted by positions at  $t$  and  $t - \delta t$  in the previous equation.

### 3.2 Leap-frog method

Given some of the shortcomings of the Verlet algorithm, Hockney proposed the Leap-Frog method. The Leap-Frog method was derived from the Verlet method. It gets the speed in half an integral time and uses this speed to calculate the new position. The position and speed expressions are

$$\begin{cases} \vec{v}_i\left(t + \frac{1}{2}\delta t\right) = \vec{v}_i\left(t - \frac{1}{2}\delta t\right) + \vec{a}_i(t)\delta t \\ \vec{r}_i\left(t + \delta t\right) = \vec{r}_i(t) + \vec{v}_i\left(t + \frac{1}{2}\delta t\right) \end{cases} \quad (5)$$

When calculating, assuming  $\vec{v}_i\left(t - \frac{1}{2}\delta t\right)$  and  $\vec{r}_i(t)$  are known, the force and acceleration  $\vec{a}_i(t)$  of the particle are calculated by the position  $\vec{r}_i(t)$  at  $t$ , and then the velocity  $\vec{v}_i\left(t + \frac{1}{2}\delta t\right)$  at the moment  $t + \frac{1}{2}\delta t$  is predicted.

According to the time available for the time being

According to  $\vec{v}_i\left(t + \frac{1}{2}\delta t\right)$  and  $\vec{v}_i\left(t - \frac{1}{2}\delta t\right)$ , the velocity at time  $t$  can be calculated:

$$\vec{v}_i(t) = \frac{1}{2}[\vec{v}_i\left(t + \frac{1}{2}\delta t\right) + \vec{v}_i\left(t - \frac{1}{2}\delta t\right)] \quad (6)$$

The use of Leap-Frog method only needs to store  $\vec{v}_i\left(t - \frac{1}{2}\delta t\right)$  and  $\vec{r}_i(t)$  these two types of information, which can save storage space and enhance the accuracy and stability at the same time. The Leap-Frog method does not need to calculate the next position to get the speed, but it is important to note that the speed is not defined at the same time as the position, and the result is that the kinetic energy and potential energy are not defined at the same time. So the total energy cannot be calculated directly.

### 3.3 Velocity Verlet method

One of the problems with the Verlet algorithm described above is that the position and speed of the current time cannot be obtained at the same time, so that kinetic energy, temperature and other information cannot be obtained in the current state. This is inconvenient in the actual integration process. In practical applications, Velocity Verlet is a more practical method, which is widely used in molecular dynamics simulation software. This method can get the position, velocity and acceleration at the same time without sacrificing accuracy.

The equation of the location is:

$$r(t + \delta t) = r(t) + v(t)\delta t + \frac{1}{2}a(t)(\delta t)^2 \quad (7)$$

It can be seen that the position of the next moment depends only on the position at current moment, speed and acceleration.

The equation of the velocity is:

$$v(t + \delta t) = v(t) + \frac{a(t)+a(t+\delta t)}{2} \delta t \quad (8)$$

It can be seen that the speed at the next moment depends on the speed of the current moment, the acceleration and the acceleration at the next moment.

#### 4. Monte Carlo Simulation

Monte Carlo method, also known as random sampling or statistical test method, is a branch of computational mathematics, which was developed in the mid-40s of last century in order to adapt to the development of the atomic energy. The traditional method cannot be approximated to the real physical process; hence it is difficult to get satisfactory results. Monte Carlo method can simulate the actual physical process, so the problem is very consistent with the actual that people can get very satisfactory results [5].

##### 4.1 Metropolis Algorithm

Metropolis algorithm, also known as Metropolis sampling, is the basis of simulated annealing algorithm. Monte Carlo method is a stochastic simulation of the equilibrium state of a large number of atoms at a given temperature in the early scientific calculation, yet its amount of calculation is large. In 1953, Metropolis proposed the importance of sampling, that is, to accept the new state by probability, rather than the use of fully defined rules, which is known as the Metropolis criteria that can significantly reduce the amount of calculation.

Assuming that the previous state is  $x(n)$ , the system is subject to a certain disturbance and the state becomes  $x(n+1)$ ,

Correspondingly, the system energy is changed from  $E(n)$  to  $E(n+1)$

$$\begin{cases} 1, & E(n+1) < E(n) \\ \exp\left(-\frac{E(n+1)-E(n)}{T}\right), & E(n+1) \geq E(n) \end{cases} \quad (9)$$

When the state is shifted, if the energy is reduced, then the transfer is accepted (with probability 1). If the energy increases, it means that the system has deviated from the global optimal position farther away (the lowest point of energy, the location that the simulated annealing algorithm is looking for is the point with highest density and lowest energy), then the algorithm will not immediately abandon it, but will conduct probability judgment:

First, a uniformly distributed random number  $\varepsilon$  is generated in the interval  $[0,1]$ . If  $\varepsilon < p$  ( $p$  is the probability of acceptance as defined above), this transition will also be accepted, otherwise it will refuse to move into the next step. This is the Metropolis algorithm, whose core idea is when the energy increases it receives with a certain probability, rather than blindly refusing.

##### 4.2 Detailed Balance

Detailed balance, which is known as strict thermal balance, is the micro-reversible equilibrium state which is difficult to be achieved. In high-temperature gaseous plasma, atoms, ions, electrons are moving at a high speed, and constantly collide with each other.

Due to inelastic collision or absorption of the appropriate energy of the photon, the atoms can lose electrons and become ions (or ions lose electrons and become higher ionization ions), And some of the ions due to collision and radiation of a certain amount of energy photons, are combined with the electrons for the atoms; Due to collision, atoms (or ions) absorb a part of the energy to be simulated to a higher energy level, while other atoms (or ions) in the higher level transfer their extra energy to the particles collide with them due to inelastic collision and drop to a lower level.

Some atoms (or ions) absorb a certain energy of the photon and jump to a higher energy level, while others in the higher level of atoms (or ions) radiate a certain energy of the photon and spontaneously transfer to the lower level. When the above-mentioned high- temperature gaseous plasma is in the thermally dynamic equilibrium state and the radiation field energy density is not too small and the gas density is moderate, the above-mentioned positive and negative processes may be relatively stable and reach a strict balanced state. The number of each positive process is equal to the number of its inverse processes, and such equilibrium state is called detailed balance. When the high temperature gaseous plasma is in a detailed equilibrium state, it is certainly in a thermally balanced state, however, the high temperature gaseous plasma in the thermally balanced state is not always in a delicate equilibrium state.

## 5. Comparison of molecular dynamics simulations and Monte Carlo simulations

For a large number of particle systems, it is almost impossible to calculate the physical quantities of all the states involved, and then to calculate its average. And the observation is the average, how to compare the calculated values and observations?

Approximation: Assuming that the physical quantity of interest changes after the system reaches a certain scale, it does not change with the scale. Thus: a series of limited states are statistically averaged. Stochastic simulation method (MC) - Monte Carlo method; deterministic simulation method (MD) - molecular dynamics method.

MD: It is described by the equation of motion, and the static and dynamic properties of the system are obtained by statistical methods, and the macroscopic properties of the system are obtained. It can be seen as the development process simulation of the system in a period of time. There are no random factors - deterministic modeling method. Deterministic simulation method usage restrictions: In fact, the molecular dynamics simulation method and the stochastic simulation method are faced with two basic constraints: limited observation time and finite system size limit

Often people are interested in the nature of the system under thermodynamic limits (i.e., the number of particles tends to infinity). However, the size of the system allowed by computer simulations is much smaller than the thermodynamic limit, and therefore a limited size effect may occur. In order to reduce the limited size effect, people often introduce periodic, total reflection, diffuse reflection and other boundary conditions. Of course, the introduction of boundary conditions clearly affects some of the properties of the system.

The advantages of Monte Carlo (MC) method: It can more realistically describe the nature of things with random properties and physical experimental process, and the subject to geometric conditions are limited, while the convergence rate has nothing to do with the number of dimensions of the problem. It has the ability to simultaneously calculate multiple solutions with multiple unknowns, the error is easy to be determined, the program structure is simple and easy to implement.

Disadvantages: convergence speed is slow; error has its probability. The results are related to the system size. [5, 9]

## 6. Conclusion

With the change of the times, the method of numerical integration algorithm in molecular dynamics simulation is more and more accurate and the previous shortcomings can be avoided. After continuous improvement and perfection, the position, velocity and other data of the particle at the given moment are not only improved, and have gradually been able to choose a different degree of corresponding numerical integration method according to people's needs, and have also significantly improved the energy conservation while improving the accuracy. It is believed that through the more rigorous calculation and derivation and the further refinement of the relevant algorithms, we can ensure that the calculation is within the acceptable range while the accuracy is improved. At the same time, by combining the molecular dynamics and Monte Carlo simulation method effectively, they can significantly simulate more complex micro-system.

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