

CHAPTER 3

MOLECULAR DYNAMICS METHOD

3.1 Introduction

Molecular Dynamics is concerned with the time evolution, under the laws of classical mechanics, of systems of particles interacting via conservative forces. From a technical point of view it is simply a numerical solution of the classical N-body problem, but its main purpose is in elucidating the equilibrium and transport properties of condensed matter.

Let us use the abbreviation Γ for a particular point in phase space, and suppose that we can write the instantaneous value of some property \mathcal{A} (it might be the potential energy) as a function $\mathcal{A}(\Gamma)$. The system evolves in time, so that Γ , and hence $\mathcal{A}(\Gamma)$ will change. It is reasonable to assume that the experimentally observable or macroscopic property \mathcal{A}_{obs} is really the time average of $\mathcal{A}(\Gamma)$ taken over a long time interval:

$$\mathcal{A}_{\text{obs}} = \langle \mathcal{A} \rangle_{\text{time}} = \langle \mathcal{A}(\Gamma(t)) \rangle_{\text{time}} = \lim_{t_{\text{obs}} \rightarrow \infty} \frac{1}{t_{\text{obs}}} \int_0^{t_{\text{obs}}} \mathcal{A}(\Gamma(t)) dt$$

In the view of computer simulation, the integration of the above equation is practically calculated for a long finite time. In fact, the equations of motion are usually solved on a step-by-step basis, i.e. a large finite number τ_{obs} of time steps, of

length $\delta t = t_{\text{obs}} / \tau_{\text{obs}}$ are taken. In this case, we may rewrite the equation into the new form

$$A_{\text{obs}} = \langle A \rangle_{\text{time}} = \frac{1}{\tau_{\text{obs}}} \sum_{\tau=1}^{\tau_{\text{obs}}} A(\tau) .$$

In the summation, τ simply stands for an index running over the succession of time.

3.2 Simulation Procedures

3.2.1 Introduction

Molecular Dynamics simulations usually consist of 2 steps. The first one is the initialization. In this step, each moving particle is either put into a regular lattice point with fixed orientation or randomly generated and given a random velocity consistent with the input temperature. The velocities are immediately renormalized so that the simulation system will have a zero net linear momentum. The simulation is then carried out with frequent renormalization of the velocities to the given input temperature. The purpose of this stage is to relax the system by removing the excessive energy through renormalization to equilibrium.

The second stage of the simulation is the continuation of the first but without renormalization of the velocities to ensure that a true equilibrium state is reached. The input temperature in Molecular Dynamics simulation is not a control parameter: in the micro-canonical ensemble the total energy, the volume, and the number of particles are constant quantities.

To perform a Molecular Dynamics simulation, the following four steps are

required:

- (i) predict the positions, velocities, accelerations etc. at the next time step;
- (ii) evaluate the forces, and hence accelerations $a_i = f_i/m_i$, from the new positions;
- (iii) correct the predicted positions, velocities, accelerations etc., using the new accelerations;
- (iv) calculate any variables of interest, such as the energy, virial, order parameters, ready for the accumulation of time averages, before returning to (i) for the next step.

All of particles used in the simulation are contained in an imaginary box with a constant density. A "periodic boundary condition" is introduced in order to overcome the problem of surface effects. The (cubic) box is replicated throughout space to form an infinite lattice. In the course of simulation, as a molecule moves in the original box, its periodic image in each of 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 thus 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 Fig 3.1. The duplicate boxes are labeled A,B,C, etc., in an arbitrary fashion. 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 use of periodic boundary condition keeps the number density in the central box (and hence in the entire system) constant. It is not necessary to store the coordinates of all the images in a simulation (an infinite number!), just those of the molecules in the central box.

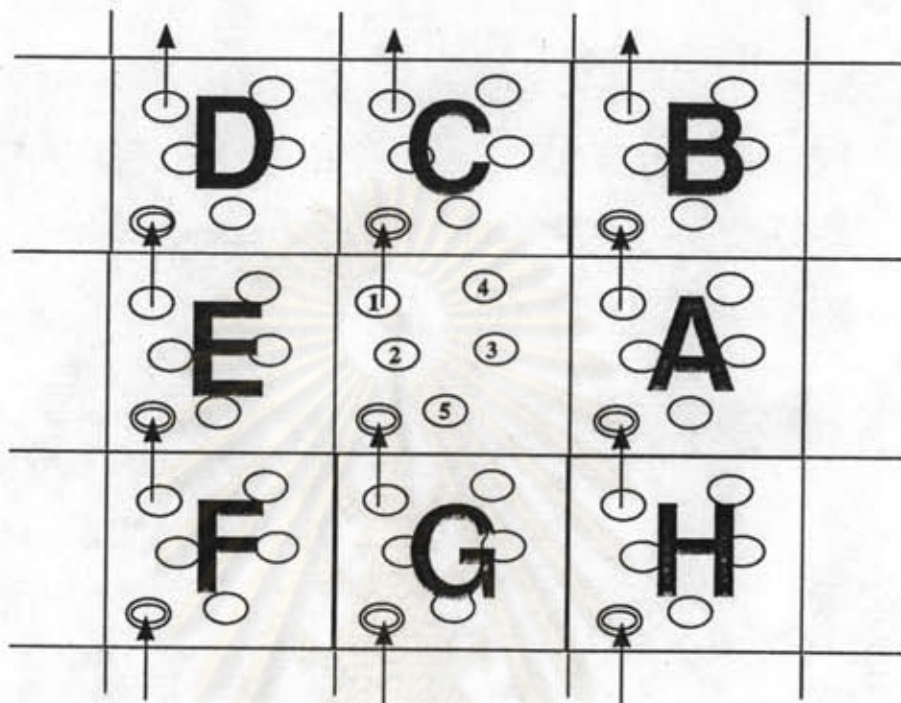


Fig 3.1 The periodic boundary condition

3.2.2 Calculation of Potentials and Forces

Molecular Dynamics simulation starts on the assumption that the motion of particles can be treated with classical dynamics according to Newton's equations of motion. For an isolated system composed of N particles, the translational motions are given by

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$



where

$$\mathbf{F}_i = -\nabla_i V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

m_i is mass and \mathbf{r}_i denotes position of the particle i . \mathbf{F} is the net force acting on the particle arising from the potential V at the instant time t . Assuming, for simplicity, a pairwise additive potential, and the absence of external forces, then

$$V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{ij} V_{ij}(r_{ij}) \quad ; \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$$

and the force acting on particle i is given by

$$\mathbf{F}_i = \sum_j \mathbf{F}_{ij}$$

where

$$\mathbf{F}_{ij} = -\mathbf{F}_{ji} = -\frac{\partial V_{ij}(r_{ij})}{\partial \mathbf{r}_{ij}}$$

Cut-off limit

In principle, the potential energy (and force) should be calculated by summing over all the interactions in the infinite periodic system [68]. In practice, the long range van der Waals interactions, proportional to R^{-6} are usually truncated at a distance of less than one-half the box-length, called cut-off limit, r_c . Therefore, for

each pair interaction only the nearest image needs to be considered in calculating the potential energies and forces [69]. However, this approximation breaks down for a very long-range Coulombic interaction. Fortunately, this study employs an infinitely dilute system which contains only one ion, and due to these corrections for the long-range interactions have not to be performed.

Shifted-force/potential method

The truncation of the intermolecular potential at the cut-off limit introduces some difficulties in defining a consistent potential and force, i.e., of the function $V(r_{ij})$ discontinuity at $r_{ij} = r_c$. Whenever a pair of molecules crosses this boundary, the total energy will not be conserved. To avoid this, the shifted-force/potential method is introduced; the potentials have been changed as the following expression:

$$V^{SF}(r_{ij}) = \begin{cases} V(r_{ij}) - V_c - \left(\frac{dV(r_{ij})}{dr_{ij}} \right)_{r_{ij}=r_c} (r_{ij} - r_c) & r_{ij} \leq r_c \\ 0 & r_{ij} > r_c \end{cases}$$

where $V^{SF}(r_{ij})$ and V_c are the shifted potential and potential at cut-off limit, respectively. By this way, the force goes smoothly to zero at the cut-off limit, removing problems in energy conservation and any numerical instability in the equations of motion.

Neighbouring algorithm

Although the cut-off limit leads to the reduction of time to calculate forces

and potential, it still needs time to examine all pair separations whether they are within cut-off limit. The amount of time used is proportional to N^2 . Verlet [70] suggested a technique for improving the speed of a program by maintaining a list of the neighbours of a particular molecule, which is updated at intervals. During updating of the neighbour list, the program does not check through all the j molecules, but just those appearing on the list.

The Predictor-Corrector Algorithm

To perform the motions of particles in Molecular Dynamics simulation, one of the finite difference methods namely the predictor-corrector routine is selected. The trajectories of particles are assumed to be continuous, then an estimate of the positions, velocities etc. at time $t+\delta t$ may be obtained by Taylor expansion :

$$r^P(t+\delta t) = r(t) + \delta t v(t) + \frac{1}{2} \delta t^2 a(t) + \frac{1}{6} \delta t^3 b(t) + \dots$$

$$v^P(t+\delta t) = v(t) + \delta t a(t) + \frac{1}{2} \delta t^2 b(t) + \dots$$

$$a^P(t+\delta t) = a(t) + \delta t b(t) + \dots$$

$$b^P(t+\delta t) = b(t) + \dots$$

The superscript marks these as 'predicted' values: r , v , a , and b stand for the set of positions, velocities, accelerations and the third derivatives of r . After the motions have been done, the correct accelerations $a_c(t+\delta t)$ can be calculated and then compared to the predicted value $a^P(t+\delta t)$ to estimate the size of error in the prediction step:

$$\Delta a(t+\delta t) = a^c(t+\delta t) - a^P(t+\delta t).$$

This error, and the results of the predictor step, are fed into the corrector step, which reads, typically,

$$r^c(t+\delta t) = r^p(t+\delta t) + c_0 \Delta a(t+\delta t)$$

$$v^c(t+\delta t) = v^p(t+\delta t) + c_1 \Delta a(t+\delta t)$$

$$a^c(t+\delta t) = a^p(t+\delta t) + c_2 \Delta a(t+\delta t)$$

$$b^c(t+\delta t) = b^p(t+\delta t) + c_3 \Delta a(t+\delta t)$$

The idea is that $r^c(t+\delta t)$ etc. are now better approximations to the true positions, velocities etc. Gear [71,72] has discussed the 'best' choice for the coefficients $c_0, c_1, c_2, c_3 \dots$

Verlet [70] proposed a method to predict more accurate positions, velocities etc. using the previous positions:

$$r(t+\delta t) = 2r(t) - r(t-\delta t) + \delta t^2 a(t).$$

3.2.3 Calculating Macroscopic Properties

(i) Static properties

Translational kinetic (K_{tr}) and *potential energies* (V) of the system can be easily calculated by:

$$K_{tr} = \left\langle \frac{1}{2} \sum_i^N m_i \dot{r}_i^2 \right\rangle$$

and

$$V = \left\langle \frac{1}{2} \sum_i^N \phi_i \right\rangle$$

where $\langle \dots \rangle$ averages over the time steps, N is the number of molecules in the system, ϕ_i and m_i are the potential energy and mass of molecule i .

The internal *pressure* of the system is calculated from the virial theorem:

$$P = (Nk_B T + W)$$

where W is the virial of the system,

$$W = -\frac{1}{3} \left\langle \sum_1^N r_i \frac{\partial \phi_i}{\partial r_i} \right\rangle = -\frac{1}{3} \left\langle \sum_1^N \sum_{j>1}^N r_{ij} \frac{\partial \phi_{ij}}{\partial r_{ij}} \right\rangle$$

One of the most important static properties is the pair *radial distribution function* (RDF), since it expresses the structure of the solvation shell or solvent structure. The RDF, usually written as $g_{\alpha\beta}(r)$, gives the probability of finding particle β at the distance r away from particle α . The function is usually normalized to 1 at large r . The RDF can be calculated by dividing the interval within $r=0$ and $r=r_c$ into segments of

size δr and counting the number of atomic pairs (α, β) with distance falling in a given range. The results are averaged over different time steps. Let $N(\Delta r)$ be the number of pairs which are r_i to $r_i + \delta r$ apart, then

$$g_{\alpha\beta}(r) = \frac{\mathcal{V}}{N} \left\langle \frac{N(\Delta r)}{4\pi r^2 \delta r} \right\rangle$$

where \mathcal{V} is the simulation volume.

(ii) Dynamic properties

Dynamic properties are most conveniently studied via the time correlation function which relates a property A at a original time to a property B at a later time. It is calculated at discrete time steps according to:

$$\langle A(0)B(t) \rangle = \langle A(t_0)B(t_0+t) \rangle_{t_0}$$

where $A(t)$ and $B(t)$ are dynamical variables of the system, such as position, velocity, density, etc. The time average in this case denotes an averaging over different time origins t_0 within a simulation run.

The *velocity autocorrelation function*,

$$C_v(t) = \langle v_i(0) \cdot v_i(t) \rangle$$

is often of great interest because its time integral relates to the self diffusion coefficient, whereas its temporal Fourier transform is a measure of the 'density of states'. The *self-diffusion coefficient* D obtained from the velocity autocorrelation

function can be written in the form:

$$D = \frac{1}{3} \int_0^{\infty} C_{vv}(t) dt$$

3.3 Specification of the Model for this Study

Four kinds of systems were studied by Molecular Dynamics simulation. The first two simulations were performed at the temperature of 235 K and 266 K using the Zn(II)-NH₃ intermolecular pair potential. The latter two were performed at the same temperatures using the Zn(II)-NH₃ intermolecular pair potential including three-body corrections. Each system consisted of one Zn(II) and 215 NH₃ at atmospheric pressure.

Table 3.1 Simulation details of this work

Zn(II)-NH ₃ potential	temperature K	density g/cm ³	box length Å
pair	235	0.688	20.66
pair	266	0.648	21.08
pair+three-body corr.	235	0.688	20.66
pair+three-body corr.	266	0.648	21.08