

MOLECULAR DYNAMICS

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1 Introduction

We carry out computer simulations in the hope of understanding the properties of assemblies of molecules in terms of their structure and the microscopic interactions between them. The two main families of computer simulation technique are Molecular Dynamics (MD) and Monte Carlo (MC). The obvious advantage of the former over latter is that it can simulate the dynamics of particles, which gives a route to dynamical properties of the system: transport coefficients, eg. thermal conductivity.

Computer simulations act as a bridge between theory and experiment (Fig. 1). We may test a theory by conducting a simulation using the same model. We may also test the model by comparing with experimental results. Besides, we may carry out simulation on the computer that are difficult or impossible to be carried out in the laboratory, eg. working at extreme of temperature or pressure.

In this lecture, we shall concentrate on molecular dynamics simulation (in 2D ¹). Molecular dynamics simulation is widely used for studying classical many-particles systems. Basically, it integrates the equations of motion of the system numerically.

2 Methodology

For each atom i , we have the equations of motion :

$$\begin{aligned}\frac{dx_i}{dt} &= v_{x,i} \\ \frac{dv_{x,i}}{dt} &= a_{x,i} \\ \frac{dy_i}{dt} &= v_{y,i} \\ \frac{dv_{y,i}}{dt} &= a_{y,i}\end{aligned}\tag{1}$$

where $v_{x,i}$ and $v_{y,i}$ are the components of the velocity of the i^{th} atom, which is located at position (x_i, y_i) , and $a_{x,i}$ and $a_{y,i}$ are the components of the acceleration of the i^{th} particle, which is determined by the forces from all the other particles in the system.

¹Although an extension to 3D is just straightforward

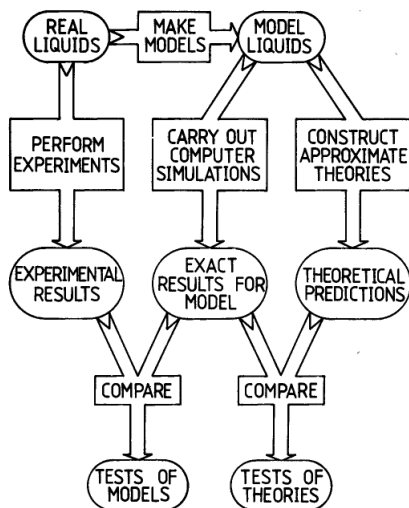


Figure 1: The connection between experiment, theory, and computer simulations

2.1 Verlet Algorithm

In nearly all the problems we have encountered so far, the Euler method has been enough. However, in MD we will be interested in computing the motion over a very large number of time steps, and it turns out that the numerical errors associated with Euler method are too big to tolerate. Therefore, it is necessary to employ other scheme for solving the equations of motion, i.e. Verlet method, which has smaller numerical errors associated compared with Euler method. Letting x_i , $v_{x,i}$ and $a_{x,i}$ be the x components of position, velocity and acceleration of particle i at time-step t , their values at the next time step are given according to the **Verlet algorithm** as :

$$\begin{aligned}
 x_i(t+1) &\approx 2x_i(t) - x_i(t-1) + a_{x,i}(t)(\Delta t)^2 \\
 v_{x,i} &\approx \frac{x_i(t+1) - x_i(t-1)}{2\Delta t}
 \end{aligned}
 \tag{2}$$

with similar equations for y_i and $v_{y,i}$.

2.2 Interaction Potential

Newton's second law tells :

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i \tag{3}$$

where m_i is the mass for atom i and $\ddot{r}_i^2 = \dot{x}_i^2 + \dot{y}_i^2$ in 2D case. To estimate the force between any two particles (i and j) requires the knowledge of the interaction potential $U(r_{i,j})$:

$$\mathbf{F}_{i,j} = -\frac{\partial}{\partial \mathbf{r}} U(\mathbf{r}_{i,j}) \tag{4}$$

where $r_{i,j}$ is the separation of the particles. In this lecture, we shall concentrate on Lennard-Jones (LJ) potential, which is the most commonly used potential. This potential

Table 1: Reduced unit for Lennard-Jones

Quantity	Unit	Conversion
distance	σ	$x^* = x/\sigma$
time	τ	$\tau = t^* = t\sqrt{\epsilon/m/\sigma^2}$
energy	ϵ	$E^* = E/\epsilon$
velocity	σ/τ	$v^* = v\tau/\sigma$
force	ϵ/σ	$F^* = F\sigma/\epsilon$
temperature	ϵ/k_B	$T^* = Tk_B/\epsilon$
pressure	ϵ/σ^3	$P^* = P\sigma^3/\epsilon$

was used in the earliest studies of the properties of liquid argon.

$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \quad (5)$$

where ϵ and σ are constant parameters that set the energy and distance scales associated with the interaction. $\epsilon/k_B = 119.8$ and $\sigma = 3.405\text{\AA}$ are the optimised parameters for argon.

It is convenience to use reduced units when dealing with LJ potential, since m , k_B , ϵ and σ are all equal to unity in LJ reduced unit. Table 1 shows the reduced units for Lennard-Jones.

2.3 Periodic Boundary Conditions

Before we discuss the programming, there is one more issue that must be addressed, i.e. the boundary conditions. Perhaps the most obvious way to enclose the particles is in a box with hard, perfectly reflecting walls. However, the problem with this approach is that for presently available computers we are limited to systems containing a relatively small number of atoms. In small systems, the collisions with the walls can be significance to the total number of collision, in contrast to a real system, where the behavior would be dominated by collisions with other particles. Ultimately, we do not want the container affect our simulation results. Hence, it is reasonable to introduce periodic boundary conditions (PBC) to the system. To view PBC, imagine when a particle encounter a wall, it is transported instantly to the opposite side of the system, as shown in Fig. 2.

3 Exercises - hands-on simulation

We have already discuss the method, now it is time for us to work on some exercises.

Exercise 1 - Initializing a molecular dynamics simulation

- Choose the number of particles (N), and set the time interval (Δt) and the total time steps.

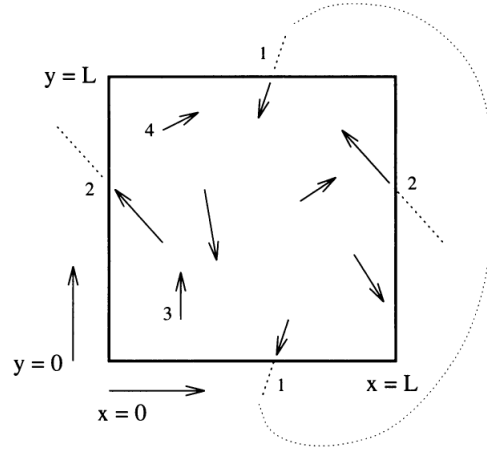


Figure 2: Periodic Boundary Conditions

- Set the initial positions and velocities of the particles:
 - Set max position component deviation dr from the vertices of a regular array.
 - Set max initial velocity component magnitude v_0 .
 - Iterate through N particles :
 - * Calculate the equidistant grid point coordinates $(g_x(i), g_y(i))$ for particle i .
 - * Displace the particle randomly a bit by setting $x(i, 1) = g_x(i) + 2(Random - 0.5)dr$, $y(i, 1) = g_y(i) + 2(Random - 0.5)dr$.²
 - * Calculate a randomized initial velocity by $v_x(i, 1) = 2(Random - 0.5)v_0$, $v_y(i, 1) = 2(Random - 0.5)v_0$.
- To set the stage for Verlet method calculations, define the fictitious position to this initial time by $x(i, 0) = x(i, 1) - v_x(i, 1)dt$, $y(i, 0) = y(i, 1) - v_y(i, 1)dt$.
- Visualize the generated initial positions of atoms.

After initializing the particle positions and velocities, the Verlet method can be used to calculate the subsequent motion of each atom. The acceleration components of i^{th} particle, $a_{x,i}$ and $a_{y,i}$, can be obtained from the Lennard-Jones potential :

$$\begin{aligned}
 a_{x,i} &= \sum_{i \neq j} \left(\frac{48}{r_{i,j}^{13}} - \frac{24}{r_{i,j}^7} \right) \cos\theta_{i,j} & (6) \\
 &= \sum_{i \neq j} \left(\frac{48}{r_{i,j}^{14}} - \frac{24}{r_{i,j}^8} \right) \Delta x_{i,j} \\
 a_{y,i} &= \sum_{i \neq j} \left(\frac{48}{r_{i,j}^{13}} - \frac{24}{r_{i,j}^7} \right) \sin\theta_{i,j} \\
 &= \sum_{i \neq j} \left(\frac{48}{r_{i,j}^{14}} - \frac{24}{r_{i,j}^8} \right) \Delta y_{i,j}
 \end{aligned}$$

²I use 1 to represent initial/first time step

where $\Delta x_{i,j}$ and $\Delta y_{i,j}$ are the components of the separation ($r_{i,j}$) between particles i and j . There are a few things which I would like to point out here :

1. We have assumed that $m = \epsilon = \sigma = 1$ so that we are using reduced units as mentioned earlier.
2. When measuring $r_{i,j}$, it must be associated with the 'minimum' separation rule of periodic boundary conditions.
3. Acceleration is calculated at each time step and this is the most time-consuming part. In order to reduce the time consumed, we therefore skip the calculation for $r_{i,j} > r_{cutoff}$, since the force is approximately equal to zero when $r_{i,j} > 3$, which can be seen from the gradient of the potential curve.

Exercise 2 - Calculation

- Iterate through N particles ($i = 1, 2, \dots, N$) and calculate the new position and velocity for each particle.
 - Calculate the distance r_{ij} to particle j (taking the periodic boundary condition into account).
 - If $r_{ij} > r_{cutoff}$, skip j .
 - Otherwise, calculate the force F_{ij} on particle i due to j . Add this force vector to the net force $F(i)$ on i from all the other particles.
 - Use the net force to update the position and velocity of particle i (take $m_i = 1$)
- :
- * $x(i, t + 1) = 2x(i, t) - x(i, t - 1) + a_x dt^2$,³
 $y(i, t + 1) = 2y(i, t) - y(i, t - 1) + a_y dt^2$.
 - * If the new position falls outside of the system, apply periodic boundary condition and bring it back inside.
 - * $v_x(i, t) = [x(i, t + 1) - x(i, t - 1)] / (2dt)$;
 $v_y(i, t) = [y(i, t + 1) - y(i, t - 1)] / (2dt)$.

4 Equilibrium State

Perhaps the most fundamental issue is whether our system reaches a proper equilibrium state.

To answer this question, we can plot a graph of energy versus time step, and see the its fluctuation. If our system is in an equilibrium state, the energy should fluctuates around a constant value, \bar{E} .

Exercise 3 - Energies versus time steps

³t denotes time step

Plot a graph of kinetic energy, potential energy and total energy versus time steps, and visualize their fluctuations. Is the system describes a microcanonical (constant energy) ensemble?

4.1 Velocity Distributions

Alternatively, to answer this question, we will focus on the behavior of the particle velocities, since we know that in equilibrium, a classical gas is described by the Maxwell distribution. For a 2-D gas, we have the *speed* distribution :

$$P(v) = C \frac{v^2}{k_B T} \exp\left(-\frac{mv^2}{2k_B T}\right) \quad (7)$$

where $P(v)$ is the probability per unit v of finding a particle with speed v , and C is a constant that depends on the mass of the particle. The corresponding *velocity* distribution is

$$P(v_x) = \frac{C_x}{(k_B T)^{\frac{1}{2}}} \exp\left(-\frac{mv_x^2}{2k_B T}\right) \quad (8)$$

with a similar expression for $P(v_y)$. If the molecular dynamics method describes the behavior of a real gas, it should yield velocity and speed distributions that have the Maxwell forms.

It is now time to do an exercise to justify the statements above.

Exercise 4 - Velocity Distributions

- Initially, all of the particles were given a velocity component whose magnitude was unity ($v = 1$ in reduced unit) and whose direction was random.
- Let the simulation run, and the velocities for all atoms and all time steps was recorded in an array.
- The speed distribution was recorded by dividing the v range into bins and tabulating the number of atoms whose speed was in the range corresponding to each bin.

4.2 Equipartition Theorem

An important quantity for a system in thermal equilibrium is the temperature, T . T does not enter the simulations as an input parameter, instead, it must be 'measured'. The results for the speed and velocity distributions can be used to measured T by fitting the curve (results) to Maxwell distribution. To make it clear, we 'adjust' the T in the Maxwell equations so that the equation shows 'exact' distribution.

Another approach is to make use of the equipartition theorem. Equipartition theorem states that *for a classical system an average energy of $\frac{1}{2}k_B T$ is associated with any degree of freedom that enters the energy quadratically*. The kinetic energy of an atom in our 2-D

system is $\frac{1}{2}m(v_x^2 + v_y^2)$, so the equipartition theorem tells us that for a system in thermal equilibrium

$$k_B T = \langle \frac{1}{2}m(v_x^2 + v_y^2) \rangle . \quad (9)$$

Here the angular bracket ($\langle \rangle$) can be interpreted in two ways. According to one point of view, Eq. 9 applies to each atom in the system, so we can obtain T by computing the *time average* of the kinetic energy of one particular atom. However, since the atoms are all equivalent, the same result can be obtained by *averaging over the different atoms* in the system at a particular instant in time. In practice the best computational accuracy will be obtained by combining the two points of view and computing the *time average of the kinetic energy per atom averaged over all of the atoms*.

Assignments

1. Briefly explain Equipartition Theorem and show its formula (similar to Eq. 9) in **3-D** case (ignore rotational degree of freedom).
2. Compare the temperature calculated from Equipartition Theorem (Eq. 9) with the value obtained by fitting the Maxwell distribution functions directly to the results in Exercise 4.