Topic 2: Molecular Dynamics of Lennard-Jones System

Molecular Dynamics (MD) is widely used to simulate many particle systems ranging from solids, liquids, gases, and biomolecules on Earth, to the motion of stars and galaxies in the Univers.

Newton's equations of motion for the system are integrated numerically. If the system is in equilibirium, static properties such as temperature and pressure are measured as averages over time. Dynamical properties such as heat transport, or relaxation of systems far from equilibrium, can also be studied.

MD simulation of Argon

One of the earliest successful MD simulations was done in 1964 by Rahman on the properties of liquid argon. His work was extended by Verlet whose improvements, especially the Verlet integration algorithm and particle neighbor lists, are widely used today.

Consider N atoms of argon each with mass $m = 6.69 \times 10^{-26}$ kg. Argon is an *inert gas*: argons atoms behave approximately like hard spheres which attract one another with weak van der Waals forces. The forces between two argon atoms can be approximated quite well by a Lennard-Jones potential energy function:

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

where r is the distance between the centers of the two atoms, $\varepsilon = 1.654 \times 10^{-21}$ J is the strength of the potential energy, and $\sigma = 3.405 \times 10^{-10}$ m is the value of r at which the energy is zero. The potential has its minimum $U(\sigma) = -\varepsilon$ at $r = 2^{1/6}\sigma = 3.822 \times 10^{-10}$ m.
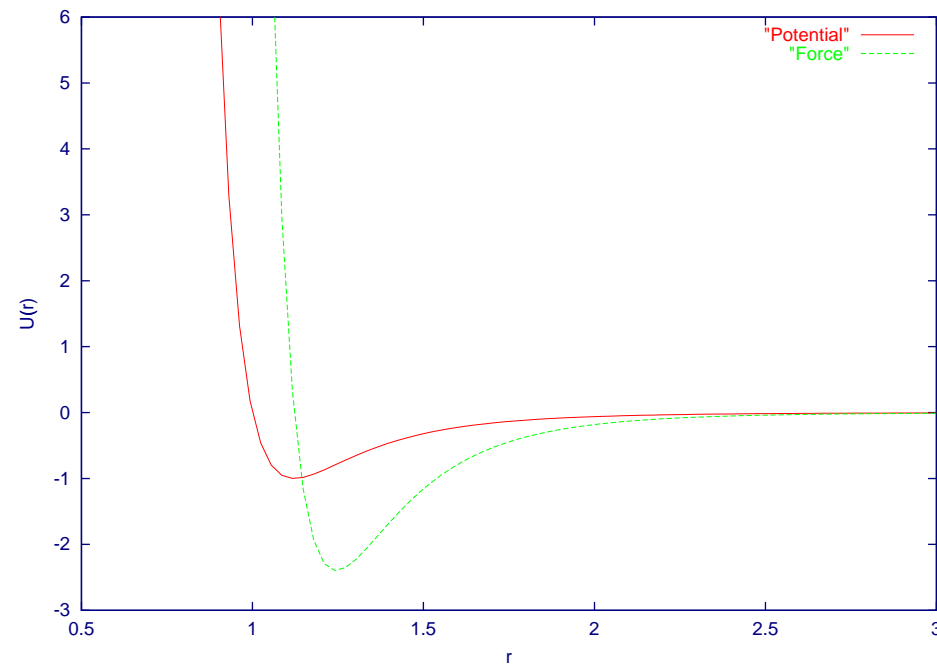
The shape of the potential and the strength of the Lennard-Jones force

$$F(r) = -\frac{dU(r)}{dr} = \frac{24\varepsilon}{\sigma}\left[2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^{7}\right],$$

are shown in the figure.

We will choose units of mass, length and energy so that $m = 1$, $\sigma = 1$, and $\varepsilon = 1$. The unit of time in this system is given by

$$\tau = \sqrt{\frac{m\sigma^2}{\varepsilon}} = 2.17 \times 10^{-12}\,\text{s}\,,$$

which shows that the natural time scale for the dynamics of this system is a few picoseconds!

Newton's Equations of Motion

The vector forces between atoms with positions $\mathbf{r}_i$ and $\mathbf{r}_j$ are given by

$$\mathbf{F}_{\text{on } i \text{ by } j} = -\mathbf{F}_{\text{on } j \text{ by } i} = 24(\mathbf{r}_i - \mathbf{r}_j)\left[2\left(\frac{1}{r}\right)^{-14} - \left(\frac{1}{r}\right)^{-8}\right]\,,$$

where $r = |\mathbf{r}_i - \mathbf{r}_j|$.

The net force on atom i due to all of the other $N - 1$ atoms is given by

$$\mathbf{F}_i = \sum_{\substack{j=1 \\ j \neq i}}^{N} \mathbf{F}_{\text{on } i \text{ by } j}\,.$$

The equation of motion for atom i is

$$\mathbf{a}_i(t) \equiv \frac{d\mathbf{v}_i(t)}{dt} = \frac{d^2\mathbf{r}_i(t)}{dt^2} = \frac{\mathbf{F}_i}{m}\,,$$

where $\mathbf{v}_i$ and $\mathbf{a}_i$ are the velocity and acceleration of atom i. These $3N$ second order ordinary differential equations (ODE's) have a unique solution as function of time t if *initial conditions*, that is, the values of positions $\mathbf{r}_i(t_0)$ and velocities $\mathbf{v}_i(t_0)$ of the particles are specified at some initial time t_0. The equations can be integrated numerically by choosing a small time step h and a discrete approximation to the equations to advance the solution by one step at a time.

Velocity Verlet Integration Algorithm

There are many algorithms which can be used to solve ODE's. Verlet has developed several algorithms which are very widely used in MD simulations. One of them is the *velocity Verlet algorithm*

$$
\begin{aligned}
\mathbf{r}_i(t+h) &= \mathbf{r}_i(t) + h\mathbf{v}_i(t) + \frac{h^2}{2}\mathbf{a}_i(t) \\
\mathbf{v}_i(t+h) &= \mathbf{v}_i(t) + \frac{h}{2}[\mathbf{a}_i(t+h) + \mathbf{a}_i(t)]
\end{aligned}
$$

It can be shown that the errors in this algorithm are of $\mathcal{O}(h^4)$, and that it is very stable in MD applications and in particular conserves energy very well.

Molecular Dynamics at constant energy

Since the Lennard-Jones forces do not depend on time, the total energy E of the system of N atoms is conserved. We will also confine the system in a fixed volume V

using periodic boundary conditions. According to the *ergodic hypothesis*, if the initial state of the system is chosen sufficiently carefully, then the successive states of the system as a function of time can be used to compute the thermal averages of various observables such as temperature and pressure. A system in thermal equilibrium at constant N, V, E is called a *microcanonical ensemble*. This type of simulation is called the *microcanonical MD method*.

The simulation algorithm consists of the following steps:

1. **Initialization:** The volume of the system and the positions and velocities of the atoms must be chosen carefully.

2. **Equilibration:** A time step h is chosen, and the equations of motion are solved iteratively for a sufficient number of steps to allow the system to come to equilibrium.

3. **Simulation:** The iterations are continued. Physical quantities are measured at each time step, and their thermal averages are computed as time averages.

Physical Observables

There are many interesting quantities that can be measured for a system in thermal equilibrium. The total energy is given by

$$E = \frac{m}{2} \sum_{i=1}^{N} \mathbf{v}_i^2 + \sum_{\text{pairs } ij} U(|\mathbf{r}_i - \mathbf{r}_j|) \, ,$$

which is the sum of kinetic and potential energies. The conservation of total energy can be monitored by measuring it. The averages of kinetic and potential energies can also be measured separately.

The absolute temperature T of a system in thermal equilibrium can be computed using Boltzmann's equipartition theorem which states that each degree of freedom of the system has associated with it $\frac{1}{2}k_{\mathrm{B}}T$ of thermal energy on average, where $k_{\mathrm{B}} = 1.38 \times 10^{-23}$ J/K is Boltzmann's constant, and T measured in Kelvins (K). Since each argon atom has three degrees of freedom (it can move in the x, y and z directions), and there are N atoms in the system,

$$N\frac{3}{2}k_{\mathrm{B}}T = \left\langle \frac{m}{2}\sum_{i=1}^{N}\mathbf{v}_i^2 \right\rangle ,$$

where $\langle \ldots \rangle$ denotes a time (ensemble) average. Thus the temperature is determined by the average kinetic energy.

Another interesting observable is the pressure P of the system. If the system is confined in a box with walls, the pressure can be estimated from the average force exerted by atoms bouncing off the walls. However, there is a more convenient way of measuring the pressure using the *virial theorem* which states that

$$PV = Nk_{\mathrm{B}}T - \frac{1}{3}\left\langle \sum_{i=1}^{N}\mathbf{r}_i \cdot \mathbf{F}_i \right\rangle .$$