

## Introduction

Molecular dynamics (MD) covers a broad class of methods in both classical and quantum physics. Classical MD involves solving Newton's equations for each particle in the simulation box, while quantum or ab-initio MD involves solving for the time dependence of atoms or nuclei by first solving Schrodinger's equation for the relevant wavefunctions. We shall concentrate on classical MD. This seems trivial in that we simply solve

$$\vec{F} = m\vec{a} = m\frac{d^2\vec{r}}{dt^2}. \quad (1)$$

for each particle or atom in the system. Nevertheless MD turns out to be very interesting in terms of algorithmic methods, applied math and in interpreting the results. The key difficulty is that we are usually interested in many particles, for example in simulating the evolution of Galaxies we need to take millions of stars, or in simulating a protein we need to take hundreds of different amino acid residues each of which has many atoms.

There are many MD packages available for a variety of different problems. For proteins and other biomolecules the standard packages are CHARM, AMBER, GROMOS... while for polymers and other materials LAMMPS is a standard. A key element in all of these packages is the force that is used. The force is found from a potential and the potential determines the type of algorithm that is used, with different methods being applied to long range as opposed to short range potentials.

An important interatomic potential in materials science, chemistry and biology is the the Lennard-Jones pair potential between two atoms and is given by,

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \quad (2)$$

This potential is accurate for inert gases, such as Argon, and makes important contributions in more complex materials. The long range attractive part is due to induced dipole-dipole interactions while the short range part is repulsive due to the overlap of the electron clouds of the two atoms.  $\epsilon$  sets the strength of the interaction while  $\sigma$  sets the range. We use rescaled units where values  $\epsilon = 1$ ,  $\sigma = 1$ , so the energy is scale by  $\epsilon$  and all lengths are scaled by  $\sigma$ . The force found

from this potential is,

$$\vec{F}(r) = -\frac{\partial V}{\partial r} \hat{r} \quad (3)$$

It is best to use Cartesian co-ordinates for your calculations.

### The Verlet algorithm

MD simulations are found by numerically integrating Newton's force law for each particle, ie.

$$\vec{F}_i = m_i \vec{a}_i = m_i \frac{d^2 \vec{r}_i}{dt^2} \quad (4)$$

in our cases all of the masses are the same and we set  $m_i = 1$ . The key to solving differential equations such as these is to choose a good procedure for writing a discrete approximation to the derivatives. There are many possibilities and their accuracy is dependent on some power of the time interval used in the discrete approximation. first derivative such as velocity may be written in three ways: the backward difference;

$$v(t) = \frac{dx}{dt} = \frac{x(t) - x(t - \delta t)}{\delta t} + O(\delta t) \quad (5)$$

the forward difference;

$$v(t) = \frac{dx}{dt} = \frac{x(t + \delta t) - x(t)}{\delta t} + O(\delta t) \quad (6)$$

and the central difference

$$v(t) = \frac{dx}{dt} = \frac{x(t + \delta t) - x(t - \delta t)}{2\delta t} + O(\delta t)^2 \quad (7)$$

Notice that the central difference has a correction of higher order than the forward or backward difference, as is seen by expanding the right hand side of these equations in a Taylor series. The second derivative can be written in a similar manner, however the best form is the central differ-

ence,

$$a(t) = \frac{d^2x(t)}{dt^2} = \frac{x(t + \delta t) - 2x(t) + x(t - \delta t)}{\delta t^2} + O(\delta t)^2 \quad (8)$$

To demonstrate these equations we write the Taylor series,

$$x(t + \delta t) = x(t) + \delta t x'(t) + \frac{1}{2!} \delta t^2 x''(t) + \frac{1}{3!} \delta t^3 x'''(t) + \frac{1}{4!} \delta t^4 x''''(t) + .. \quad (9)$$

and

$$x(t - \delta t) = x(t) - \delta t x'(t) + \frac{1}{2!} \delta t^2 x''(t) - \frac{1}{3!} \delta t^3 x'''(t) + \frac{1}{4!} \delta t^4 x''''(t) + .. \quad (10)$$

Using the second derivative form in Newton's equation, we write the most basic form of the Verlet algorithm,

$$x(t + \delta t) = 2x(t) - x(t - \delta t) + \delta t^2 \vec{F}_i(t) / m_i \quad (11)$$

In order to use this equation we need the positions at two times  $x(t)$  and  $x(t - \delta t)$ . Using the central difference for the velocity, this may be written as,

$$x(t + \delta t) = 2x(t) + 2\delta t v(t) - x(t - \delta t) + \delta t^2 F(t) / m. \quad (12)$$

Writing the full set of equations, we then have,

$$\vec{x}_i(t + \delta t) = \vec{x}_i(t) + \delta t \vec{v}_i(t) + \frac{1}{2} \delta t^2 \vec{F}_i(t) / m_i \quad (13)$$

which only involves the previous time. However now we need to update  $v(t)$ . Here we use a trick, namely we use a central difference on the interval between  $t$  and  $t + \delta t$ , so that,

$$\vec{v}_i(t + \delta t) = \vec{v}_i(t) + \frac{1}{2} \delta t (\vec{F}_i(t + \delta t) + \vec{F}_i(t)) \quad (14)$$

## Project 2 - MD simulation of Argon gas (Due March 27th)

**Test of integrator:** Write an Fortran MD code using Eqs. (13) and (14) to find the motion of two atoms in a Lennard-Jones potential.

**Main Project.** Write an MD code in Fortran 90 which will simulate the motion of  $N$  atoms in a cubic box of side  $L$ . Your code should have the following features (i) periodic boundary conditions, (ii) zero center of mass momentum, (iii) a method to fix the temperature.

To check that your code is working, make sure that the energy is constant and that the momentum is conserved. Plot out a distribution of the velocities e.g.  $P(v_x)$ . What should it look like? Make a plot of the temperature as a function of time to illustrate your temperature rescaling procedure. Once the code is working and you are able to achieve a target temperature, use it to calculate the following equilibrium properties for a system of  $N=20$  or more atoms.

- The energy and specific heat as a function of temperature.
- The pair distribution function in the solid and liquid phases.
- $\langle r^2 \rangle$  vs time for the solid and liquid phases.