

Molecular Dynamics

FYS-3150

Gullik Vetvik Killie

October 19, 2014

Contents

1	Theory	2
1.1	Verlet integrator	2
1.2	Lennard-Jones Potential and force between two molecules	3
1.3	Algorithm to implement force	4
2	Useless shit	5

Notes

- Is it not the Leapfrog algorithm?
- Need to invent some unit test to implement, ask for ideas
- Dipoles? Should form crystals
- Magnetic force
- Different molecules
- Crystals mixed with liquids

1 Theory

1.1 Verlet integrator

The Integrator is a widely used integrator in molecular dynamics [2] because of its properties as a symplectic integrator which means that it conserves areas in phase space very well and it allows stable integration of the equation of motion [3]. Newton's second law for a particle in our molecule ensemble reads:

$$m \frac{\partial^2 x_i}{\partial t^2} = F_i$$

$$\frac{\partial x_i}{\partial t} = v_i \text{ and } \frac{\partial v_i}{\partial t} = \frac{F_i}{m}$$

The Leapfrog algorithm is a slight continuation on the Verlet algorithm doing the step in two steps. Doing a Taylor expansion around both the step and half the step we get.

$$x_i(t+h) = x_i(t) + hx'_i(t) + \frac{h^2}{2}x''_i(t) + \mathcal{O}(h^3) \quad (1)$$

$$x'_i(t + \frac{h}{2}) = x'_i(t) + \frac{h}{2}x''_i(t) + \mathcal{O}(h^2) \quad (2)$$

Inserting equation (2) into (1) to obtain

$$x_i(t+h) = x_i(t) + hx'_i(t + \frac{h}{2}) + \mathcal{O}(h^3) \quad (3)$$

A Taylor first order expansion of the velocity produces the following

$$x'_i(t + \frac{h}{2}) = x'_i(t) + \frac{h}{2}x''_i(t) + \mathcal{O}(h^2) \quad (4)$$

By using equation (4), then (3) and then (4) again we obtain $x_i(t+h)$ and $v_i(t+h)$. The algorithm follows:

$$\begin{aligned}
v_i(t + \frac{h}{2}) &= x'_i(t) + \frac{h}{2} \frac{F_i(t)}{m} + \mathcal{O}(h^2) \\
x_i(t + h) &= x_i(t) + hx'_i(t + \frac{h}{2}) + \mathcal{O}(h^3) \\
v_i(t + h) &= v_i(t + \frac{h}{2}) + \frac{h}{2} \frac{F_i(t + \frac{h}{2})}{m} + \mathcal{O}(h^2)
\end{aligned}$$

1.2 Lennard-Jones Potential and force between two molecules

We will be using the Lennard-Jones potential to approximate the forces between the molecules, which work quite well, given it's simplicity, for neutral particles, especially noble gases, as we are dealing with in this study [1]. The formula is given below.

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

At short distances the term to the twelfth power dominates and represents a repulsive force, Paulie exclusion principle, while at longer distances the term to sixth power dominates and represents an attractive force, van der Waal. The σ is the distance at which the potential is 0, while ϵ is the depth of the well.

Experimentally the following values for argon has been found: $\begin{cases} \epsilon/k_B &= 119.8\text{K} \\ \sigma &= 3.405\text{\AA} \end{cases}$

{ Note to self, remember that twelve is the square of six. }

The force felt between the molecules is given by the negative gradient of the potential.

$$\mathbf{F}(r_{ij}) = -\nabla U(r_{ij})$$

The potential only has a nonzero derivative along \mathbf{r}_{ij} , the axis between then particles, so it is natural to evaluate the gradient in that coordinate system before projecting it onto the xyz coordinates used by the program.

$$\begin{aligned}
\mathbf{F}(r_{ij}) &= -4\epsilon \hat{\mathbf{r}}_{ij} \partial_{r_{ij}} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \\
\mathbf{F}(r_{ij}) &= -4\epsilon \hat{\mathbf{r}}_{ij} \left[\left(-\frac{12}{\sigma} \right) \left(\frac{\sigma}{r_{ij}} \right)^{13} - \left(-\frac{6}{\sigma} \right) \left(\frac{\sigma}{r_{ij}} \right)^7 \right]
\end{aligned}$$

Then it is projected onto the xyz coordinates, $F_k = \left(F \frac{r_{ij}}{|r_{ij}|} \right)_k = F \frac{k_{ij}}{|r_{ij}|}$, where k_{ij} is the distance between the particles in direction $k = \{x, y, z\}$, and $|r_{ij}|$ is the total distance.

$$F_k = \frac{24}{\sigma} \epsilon \left[2 \left(\frac{\sigma}{r_{ij}} \right)^{13} - \left(\frac{\sigma}{r_{ij}} \right)^7 \right] \frac{k_{ij}}{|r_{ij}|}$$

1.3 Algorithm to implement force

The implementation of the force will be along the following steps:

- Calculate $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ for a particle pair
- Calculate $F_{r_{ij}} = \frac{24}{\sigma} \epsilon \left[2 \left(\frac{\sigma}{r_{ij}} \right)^{13} - \left(\frac{\sigma}{r_{ij}} \right)^7 \right]$
- Calculate $F_x = F_{r_{ij}} \frac{k_{ij}}{|r_{ij}|}$ for xyz
- Add the force to both particles force account, halves the necessary computations. One positive one negative

2 Useless shit

$$x_i(t+h) + x_i(t-h) = 2x_i(t) + h^2 x_i''(t) + \mathcal{O}(h^4)$$

$$x_i(t+h) = 2x_i(t) - x_i(t-h) + h^2 F_i(t) + \mathcal{O}(h^4) \quad (5)$$

Since we now also need the velocity at the different timesteps we will use a first order Taylor expansion to find that. To achieve the same truncation error as in the position the timestep will be halved.

$$\begin{aligned} x_i(t + \frac{h}{2}) &= x_i(t) + \frac{h}{2} x_i'(t) + \mathcal{O}\left(\frac{h^2}{2}\right) \\ x_i(t - \frac{h}{2}) &= x_i(t) - \frac{h}{2} x_i'(t) + \mathcal{O}\left(\frac{h^2}{2}\right) \end{aligned}$$

We will solve this for the velocity $v_i = x_i'(t)$ by subtracting them.

$$x_i'(t) = \frac{x_i(t+h) - x_i(t-h)}{2h} + \mathcal{O}(h^2)$$

References

- [1] Wikipedia http://en.wikipedia.org/wiki/Lennard-Jones_potential.
- [2] Morten Hjorth-Jensen. Computational physics lecture notes fall 2014.
- [3] Dominik Marx and Jurg Hutter. Ab initio molecular dynamics: Theory and implementation, 2009.