Molecular Dynamics
FYS-3150

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Contents

Notes

- Is it not the Leapfrog algorithm?
- Need to invent some unit test to implement, ask for ideas
- Is it necessary to compute potential? Analytical form of force should be enough. Loss of computing speed when not caring about potential
- 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 it's 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 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.

$$x_i(t+h) = x_i(t) + hx_i'(t) + \frac{h^2}{2}x_i''(t) + \mathcal{O}\big(h^3\big) \tag{1}$$

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

Inserting equation (2) into (1) to obtain

$$x_i(t+h) = x_i(t) + hx_i'(t+\frac{h}{2}) + \mathcal{O}\big(h^3\big) \tag{3}$$

A Taylor first order expansion of the velocity produces the following

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

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

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

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: $\begin{cases} \epsilon/k_B & = 119.8\text{K} \\ \sigma & = 3.405\text{Å} \end{cases}$

{ 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.

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

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

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

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

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.

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

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

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

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.