Project 1
Molecular Dynamics
FYS-4460

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1 Part 1:

1.1 Task e: Computing forces

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 the attractive van der Waal force. The σ is the distance at which the potential is 0, while ϵ is the depth of the well. $\sigma = 3.405$Å and $\varepsilon / k_B = 119.8$K are chosen to fit the physical properties of the system for Argon.
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.

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

$$\mathbf{F}(r_{ij}) = -4\epsilon\left[-\frac{12}{r_{ij}}\left(\frac{\sigma}{r_{ij}}\right)^{12} + \frac{6}{r_{ij}}\left(\frac{\sigma}{r_{ij}}\right)^{6}\right]\hat{\mathbf{r}}_{ij}$$

$$\mathbf{F}(r_{ij}) = 24\epsilon\left[2\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]\frac{\mathbf{r}_{ij}}{r_{ij}^2}$$

$$m_i\frac{\partial^2 r_i}{\partial t^2} = \sum_j 24\epsilon\left[2\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]\frac{\mathbf{r}_{ij}}{r_{ij}^2}$$

1.2 NonDimensionality

Now we introduce some new units to get a nondimensional equation of motion. $\begin{cases} r & \to \sigma r' \\ t & \to \tau t' \end{cases}$

$$m_i\frac{\partial^2 \sigma r'_i}{\partial(\tau t')^2} = \sum_j 24\epsilon\left[2\left(\frac{\sigma}{\sigma r'_{ij}}\right)^{12} - \left(\frac{\sigma}{\sigma r'_{ij}}\right)^{6}\right]\frac{\sigma\mathbf{r'}_{ij}}{\sigma^2 r'^2_{ij}}$$

$$\frac{\partial^2 r'_i}{\partial(t')^2} = \frac{24\epsilon\tau^2}{m_i\sigma^2}\sum_j\left[2\left(\frac{\sigma}{\sigma r'_{ij}}\right)^{12} - \left(\frac{\sigma}{\sigma r'_{ij}}\right)^{6}\right]\frac{\mathbf{r'}_{ij}}{r'^2_{ij}}$$

Choosing $\tau = \sigma\sqrt{m/\varepsilon}$ then gives the dimensionless equation

$$\frac{\partial^2 r'_i}{\partial(t')^2} = 24\sum_j\left[2r'^{-12}_{ij} - r'^{-6}_{ij}\right]r'^{-2}_{ij}\mathbf{r}'_{ij}$$

1.2.1 Algorithm to implement force

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

- Find vector between the two particles $\mathbf{r}_{ij} = \mathbf{r}'_i - \mathbf{r}_j$
- Calculate r'^2_{ij}, r'^6_{ij} and $r'^1_{ij}2$ for a particle pair
- Calculate the modified force $24\sum_j\left[2r'^{-12}_{ij} - r'^{-6}_{ij}\right]r'^{-2}_{ij}\mathbf{r}'_{ij}$
- Add the force to both particles force account, halves the necessary computations. One positive one negative

A Unit scheme

We want to use a unit system so all the numbers are computed on a unity scale, this ensures that there will be no overflow and it is easy to check that the number are approximately correct.

The program uses a more natural set of units which let's Boltzmann's constant be 1.

$$\begin{aligned}
1 \text{ mass unit } &= 39.948 \text{ a.m.u } = 39.948 \times 1.661 \times 10^{-27} \text{ kg} \quad (1)\\
1 \text{ length unit } &= 3.405 \text{ Å} = 3.405 \times 10^{-10} \text{ m} \quad (2)\\
1 \text{ energy unit } &= 1.651 \times 10^{-21} \text{ J} \quad (3)\\
1 \text{ temperature unit } &= 119.735 \text{ K} \quad (4)
\end{aligned}$$

All the other units are then expressed in term of these units.

Boltzmann constant translates between temperature and energy, in SI-units it is $k_B = 1.381 \times 10^{-23}$ J K^{-1}, which in the previously defined units becomes

$$k_B = 1.381 \times 10^{-23} \left(\text{ J K}^{-1} \right) \left(\frac{\text{energy unit}}{1.651 \times 10^{-21} \text{ J}} \right) \left(\frac{119.735 \text{ K}}{\text{temperature unit}} \right) \quad (5)$$

$$k_B = 1 \ \frac{\text{energy unit}}{\text{temperature unit}} \quad (6)$$

References

[1] Wikipedia `http://en.wikipedia.org/wiki/Lennard-Jones_potential`.