MD-Assignment 4

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1 Assignment

Structured cell simulation.

1.1 Tasks

1. Make the spline to the Lennard Jonse potential such that it is fully vanished at the prescribed distance. Check your code.
2. Introduce the cell structure that we discussed and as explained in the paper I sent you.
   - Make sure to use Newton's third law by only searching half the neighbor cells,
   - Make sure that your linked lists complete all particles and their interactions,
   - Make the cell dimensions the smallest possible such that they are larger than the potential cut-off distance.
3. With this new cell-structure code, increase the number of particles and show that your simulation time increases linearly with the number of particles.
   - Try the simulation for a given system dimension size,
   - Try simulations with a temperature around 0.75 for different numbers of particles to see that the simulated temperature is correct.
4. Implement the pressure calculation we discussed — I will send notes — and see that the pressure increases with the number of particles.
5. Ensure all of the above should be done with periodic boundary conditions.

2 Task 1: Deriving the Potential

Algorithms and relations needed for this assignment.

2.1 Spline and Lennard Jones Ensemble

We want to derive the Lennard Jones (LJ) and Spline potential which describes the energy between two bodies of particles. Ultimately from ensemble of the LJ and Spline, we can find the interaction force contribution. This interaction force can then be used for the periodic boundary and interactions between particles in a box. Here's a look at the ensemble of the potential.

Total Potential (Ensemble)

$$\phi(r) = u(r) + g(r) \tag{1}$$

where the constituent potentials are defined below

$$\text{Lennard Jones:} \quad u(r) = E_0 \left[\left(\frac{r_0}{r}\right)^{12} + \left(\frac{r_0}{r}\right)^{6} \right] \tag{2}$$

$$\text{Spline:} \quad g(r) = a(r - r_c)^2 + b(r - r_c)^3 \quad \text{for} \quad r_I \leq r < r_c \tag{3}$$

Spline Potential Derivation Required definitions and helping variables.

$$\begin{aligned}
a &= \frac{2}{3}\left(\frac{u'^2}{u}\right) \\
&= \frac{2}{3}\frac{-E_0}{r_0^2}\frac{12^2 6^2}{19 \cdot 7}\left(\frac{7}{13}\right)^{7/3} \\
&= \boxed{-6.129\left(\frac{E_0}{r_0^2}\right)} \\
b &= -\frac{4}{27}\left(\frac{u'^3}{u^2}\right) \\
&= -\frac{4}{27}\frac{E_0}{r_0^3}\frac{12^3 \cdot 6^3 \cdot 13}{19^2 \cdot 7^2}\left(\frac{7}{13}\right)^{7/2} \\
&= \boxed{-4.655\left(\frac{E_0}{r_0^3}\right)} \\
\frac{r_c}{r_0} &= \boxed{1.5475} \\
\frac{r_I}{r_0} &= \boxed{1.108}
\end{aligned}$$

We can then plug a and b into Equation 3. The final thing to do is normalize the spline potential, which is boxed in Equation 4.

$$\begin{aligned}
g(r) &= a(\Gamma - r_c)^2 + b(\Gamma - r_c)^3 \\
&= -6.129\left(\frac{E_0}{r_0^2}\right)(r - r_c)^2 + -4.655\left(\frac{E_0}{r_0^3}\right)(r - r_c)^3 \\
\frac{g(r)}{E_0} &= -6.129\left(\frac{r}{r_0} - \frac{r_c}{r_0}\right)^2 + -4.655\left(\frac{r}{r_0} - \frac{r_c}{r_0}\right)^3 \\
\frac{g(r_0\Gamma)}{E_0} &= -6.129\left(\Gamma - \frac{r_c}{r_0}\right)^2 + -4.655\left(\Gamma - \frac{r_c}{r_0}\right)^3
\end{aligned}$$

$$\boxed{\frac{g(r_0\Gamma)}{E_0} = -6.129(\Gamma - 1.5475)^2 + -4.655(\Gamma - 1.5475)^3} \quad \text{normalized potential x-direction} \tag{4}$$

When we plot the full expression of potential (Equation 1) that combines the normalized spline potential, we see Figure 1.

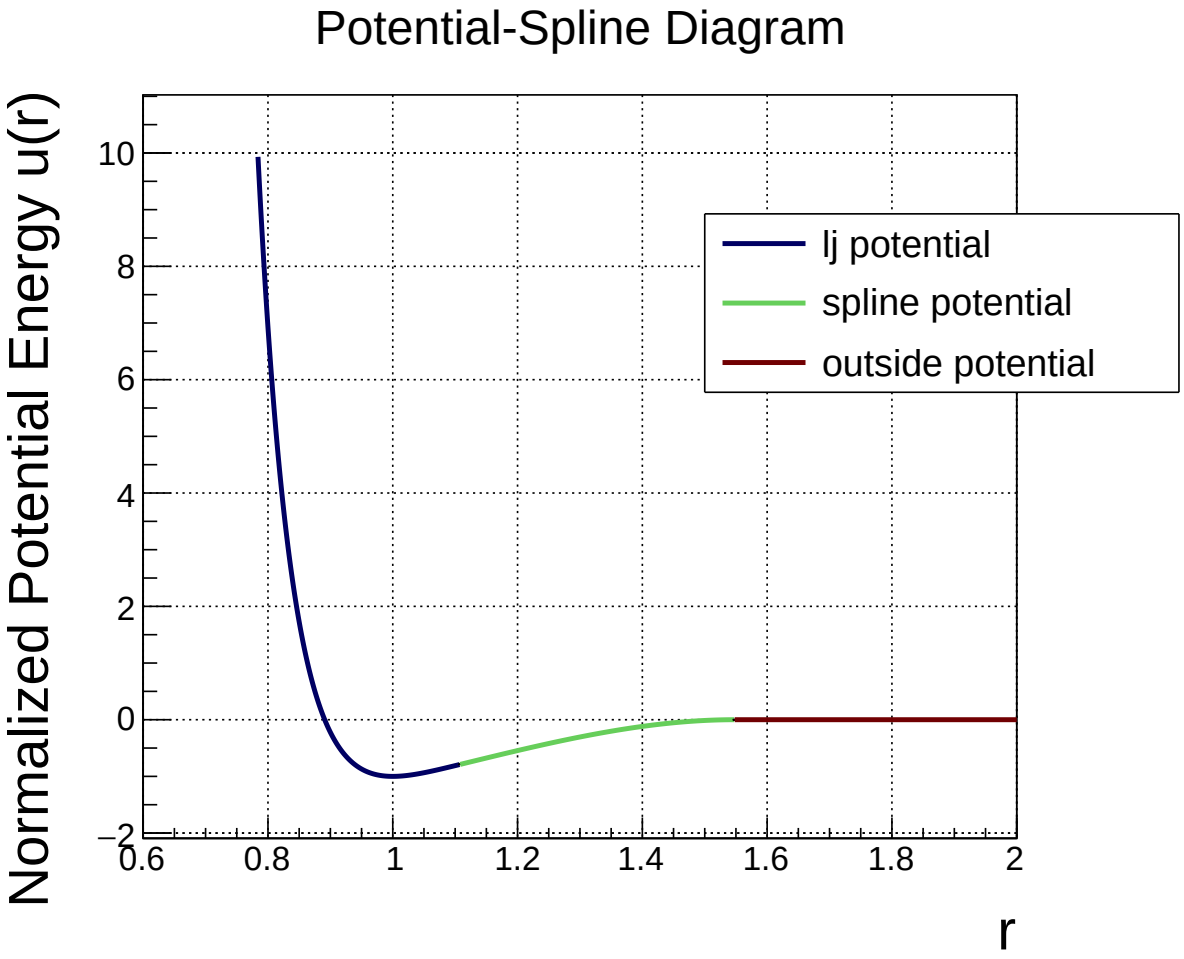

Figure 1: Visualization of LJ with spline potential (in green)

When we juxtapose the original expression (red dotted line) of the Lennard Jones potential against the new splined expression (black solid line), we see there isn't much of a difference (Figure 2). Although, the two expressions do fit together nicely.

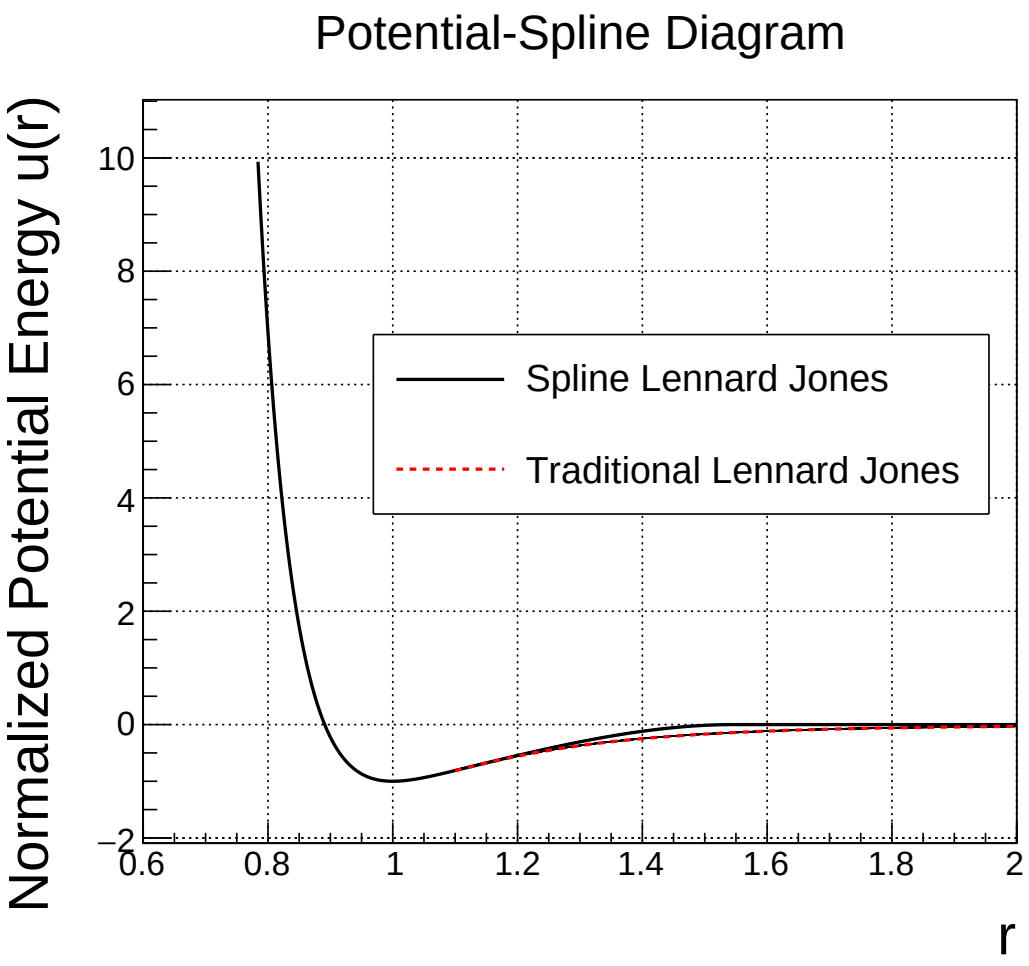

Figure 2: Comparison of Spline and Traditional

2.2 New LJ Force

The traditional Lennard Jones force in the ξ direction.

$$\begin{aligned}
\vec{\Gamma}_i &= \xi_i \hat{i} + \eta_i \hat{j} \\
\vec{\Gamma}_j &= \xi_j \hat{i} + \eta_j \hat{j} \\
|\vec{\Gamma}_i - \vec{\Gamma}_j| &= \sqrt{\xi_{ij} + \eta_{ij}} \\
\xi_{ij} &= \xi_i - \xi_j \\
\eta_{ij} &= \eta_i - \eta_j
\end{aligned}$$

Force expression.

$$\begin{aligned}
\frac{\mu d^2(\xi)}{dt^2} &= \left[\left(\frac{1}{|\vec{\Gamma}_i - \vec{\Gamma}_j|} \right)^{13} - \left(\frac{1}{|\vec{\Gamma}_i - \vec{\Gamma}_j|} \right)^{7} \right] \cdot \frac{\xi_i - \xi_j}{|\vec{\Gamma}_i - \vec{\Gamma}_j|} \\
&= \left[\left(\frac{1}{\sqrt{\xi_{ij} + \eta_{ij}}} \right)^{13} - \left(\frac{1}{\sqrt{\xi_{ij} + \eta_{ij}}} \right)^{7} \right] \cdot \frac{\xi_i - \xi_j}{\sqrt{\xi_{ij} + \eta_{ij}}}
\end{aligned}$$

Here is the force in the horizontal (ξ) direction.

$$F_\xi = \boxed{\left[\left(\frac{1}{\sqrt{\xi_{ij} + \eta_{ij}}} \right)^{13} - \left(\frac{1}{\sqrt{\xi_{ij} + \eta_{ij}}} \right)^{7} \right] \cdot \frac{\xi_{ij}}{\sqrt{\xi_{ij} + \eta_{ij}}}}$$

We will show the splie Lennard Jones force in the ξ direction. We begin with the negative derivative of the spline potential (below).

$$\begin{aligned}
-\frac{\partial g(r)}{\partial \xi} &= -2a(r - r_c)\frac{\partial r}{\partial \xi} - 3b(r - r_c)^2 \frac{\partial r}{\partial \xi} \\
&= 12.258 \left(\frac{E_0}{r_0^2} \right)(r - r_c) + 13.966 \left(\frac{E_0}{r_0^3} \right)(r - r_c)^2
\end{aligned}$$

Then we divide by the normalized force ($\frac{E_0}{r_0}$).

$$\begin{aligned}
-\frac{\frac{\partial g(r)}{\partial \xi}}{E_0/r_0} &= 12.258 \left(\frac{1}{r_0} \right)(r - r_c)\frac{\partial r}{\partial \xi} + 13.966 \left(\frac{1}{r_0^2} \right)(r - r_c)^2 \frac{\partial r}{\partial \xi} \\
&= 12.258 \left(\frac{r}{r_0} + \frac{r_c}{r_0} \right) \frac{\partial r}{\partial \xi} - 13.966 \left(\frac{r}{r_0} - \frac{r_c}{r_0} \right)^2 \frac{\partial r}{\partial \xi}
\end{aligned}$$

Let r_0 be 1. And also replace $\frac{\partial r}{\partial \xi}$ with the following.

$$\begin{aligned}
r &= \sqrt{\xi^2 + \eta^2} \\
\frac{\partial r}{\partial \xi} &= \frac{\xi}{\sqrt{\xi^2 + \eta^2}}
\end{aligned}$$

Here are the forces in the horizontal (ξ) and vertical direction (η).

$$\boxed{F_\xi = -\frac{\frac{\partial g(r)}{\partial \xi}}{E_0/r_0} = 12.258\,(r - 1.5475)\,\frac{\xi}{\sqrt{\xi^2 + \eta^2}} + 13.966\,(r - 1.5475)^2\,\frac{\xi}{\sqrt{\xi^2 + \eta^2}}} \tag{5}$$

$$\boxed{F_\eta = -\frac{\frac{\partial g(r)}{\partial \eta}}{E_0/r_0} = 12.258\,(r - 1.5475)\,\frac{\eta}{\sqrt{\xi^2 + \eta^2}} + 13.966\,(r - 1.5475)^2\,\frac{\eta}{\sqrt{\xi^2 + \eta^2}}} \tag{6}$$

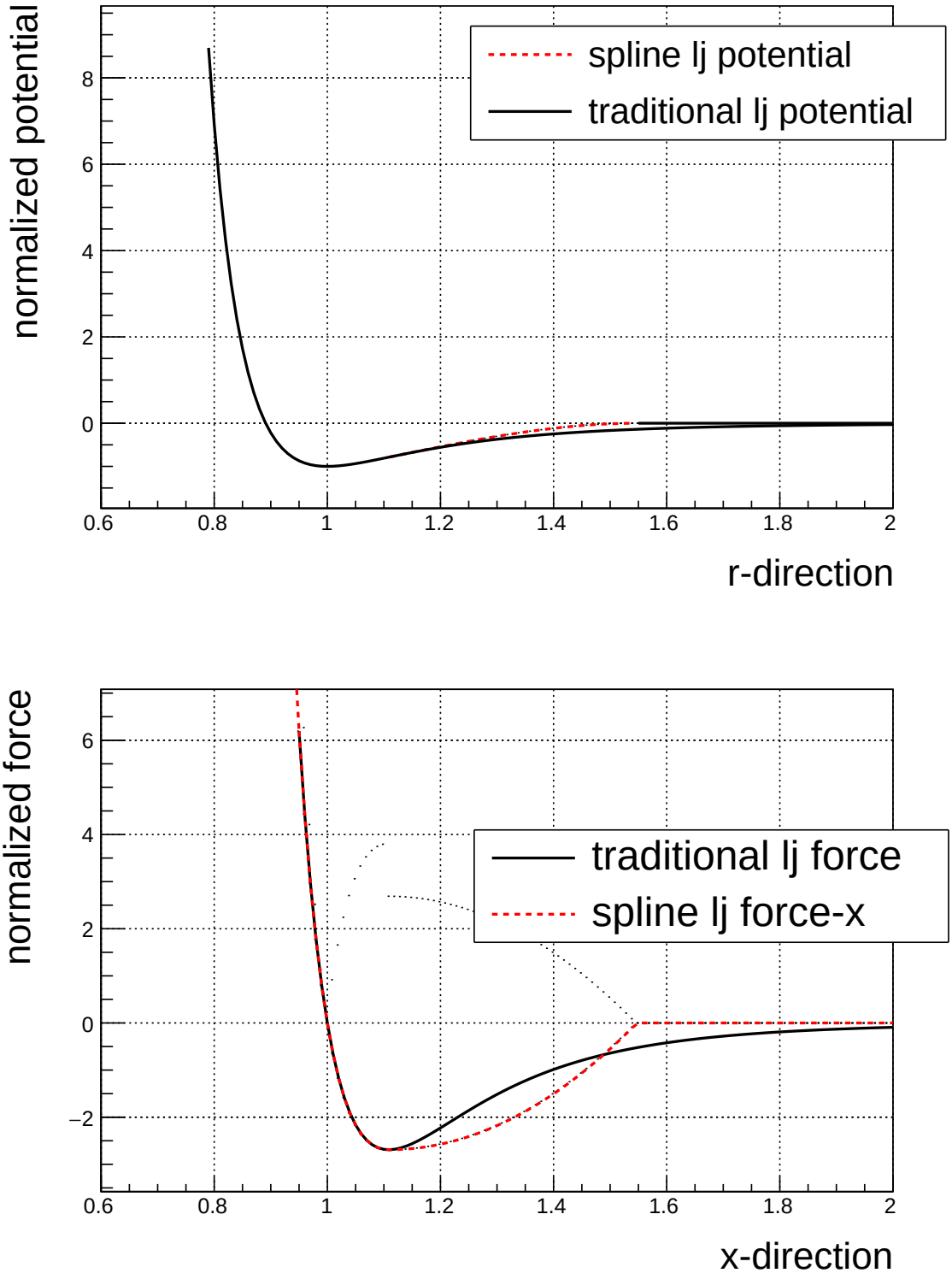

Figure 3: Comparison of Spline and Traditional Forces

The new force expression that we derived from the spline potential (shown in Figure 3) dips below equilibrium (red dotted line). So this new spline force actually interjects a pulling force for particles near enough, or within the normalized distances of 1.1 to approximately 1.5 range, but so did the traditional force. So before particle repulsion there is a pulling force.

Code implementation of the splie force.

```
def lj_force(xij,yij):
    #with spline compensation
    ri = 1.1080
    rc = 1.5475
    r  = np.sqrt(xij**2 + yij**2) #2Body Separation Distance
    ir = 1/np.sqrt(xij**2 + yij**2)

    if r<ri:
        fx = (12/r**13 - 12/r**7)*(xij*ir)
        fy = (12/r**13 - 12/r**7)*(xij*ir)
        lj = 1
        sp = 0

    if ri<=r<rc:
        fx = 12.258*((r-rc)**1)*(xij*ir) + 13.966*((r-rc)**2)*(xij*ir)
        fy = 12.258*((r-rc)**1)*(yij*ir) + 13.966*((r-rc)**2)*(yij*ir)
        lj = 0
        sp = 1
    elif r>=rc:
        fx = 0
        fy = 0
        lj = 0
        sp = 0

    return fx, fy
```

Initially I was having issues with my simulation due to an error within my splie force. Since fixing the issue I no longer have issues with divide by zero situations in which, r_{ij} became extremely low and then produced large magnitudes of forces. This caused my simulation to have trouble finding which cell an atom belonged to, especially when the atom was no longer within the box system.

3 Task 2: Cell Structure Results

The following results are for these conditions:

- α =1
- temperature(T)=10
- mass(m)=1
- Boltzmann constant(k_b)=1
- time step (dt)=0.001
- total number of time steps=5000

I chose to keep the time step fixed throughout these simulations for the best results. Previously this time step value had shown stability from the HMO system (assignment 3). Figure 4 represents the average particle energy (KE+PE) - that is also averaged with time. I plot both the kinetic energy with the full time step(V^n) and the half timestep ($V^{n+1/2}$), but they overlap each other so there was no point in including a legend to show the differences.

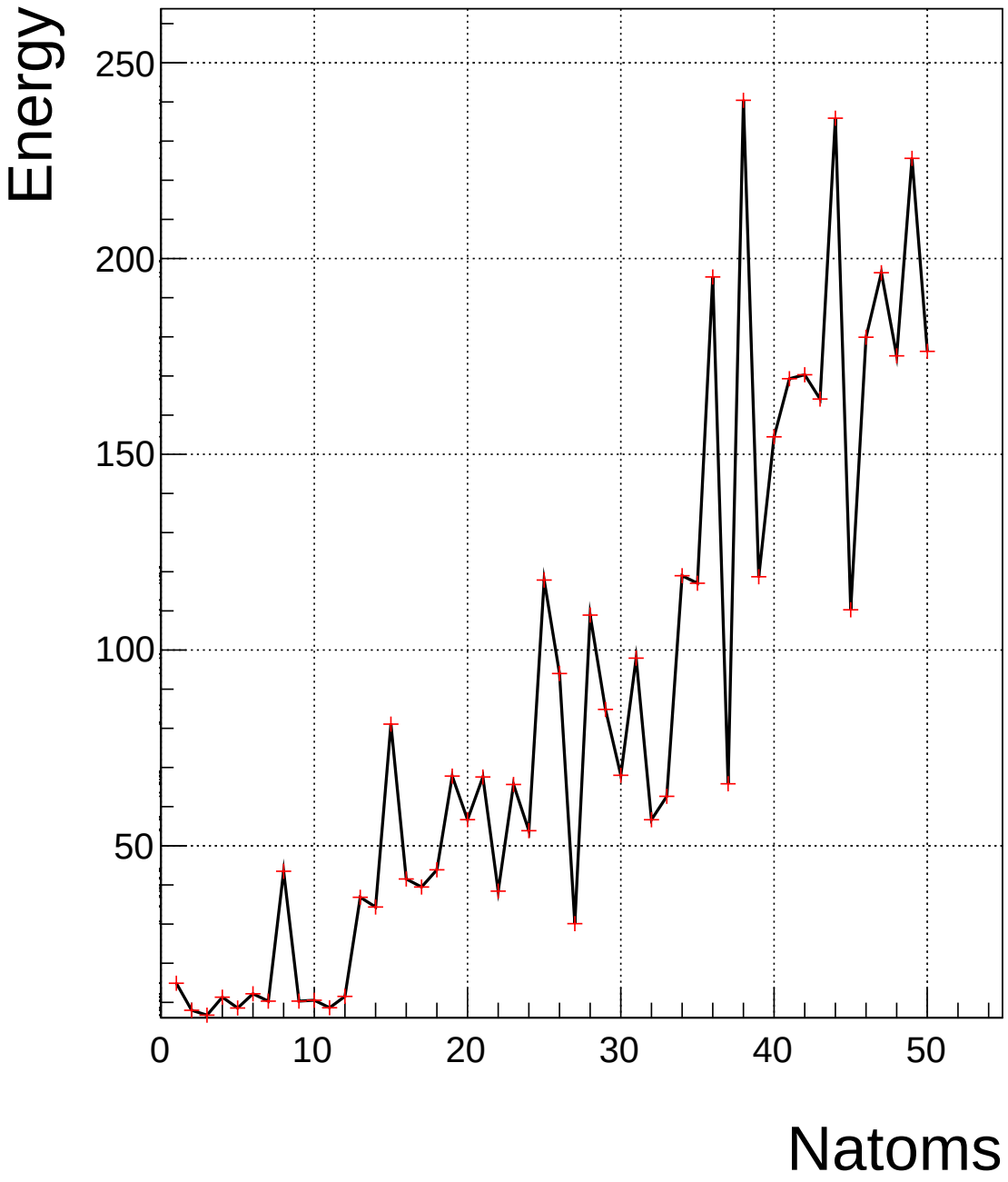

Figure 4: Average box system energy as a function of number of atoms

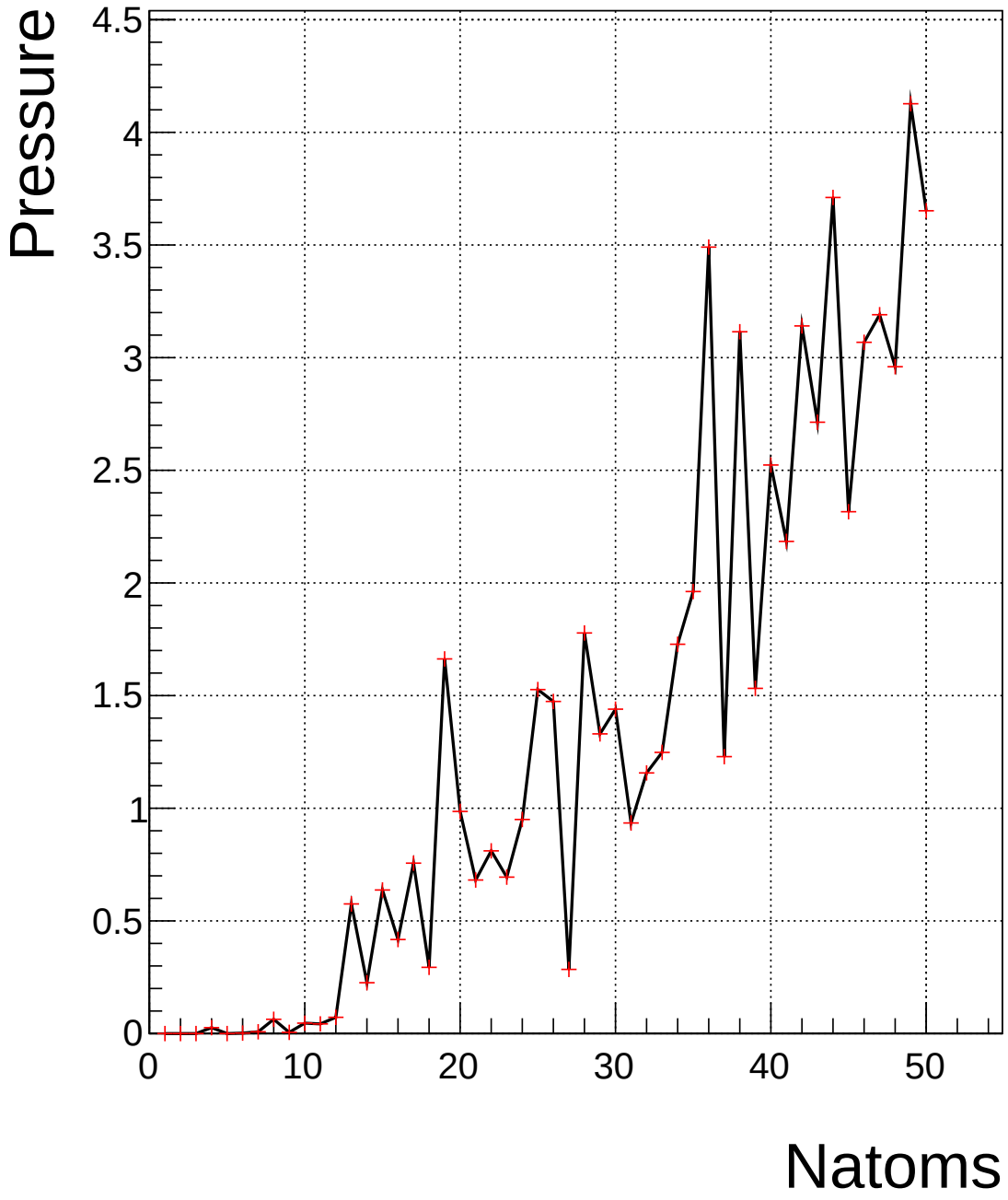

Figure 5: Average box system pressure as a function of number of atoms

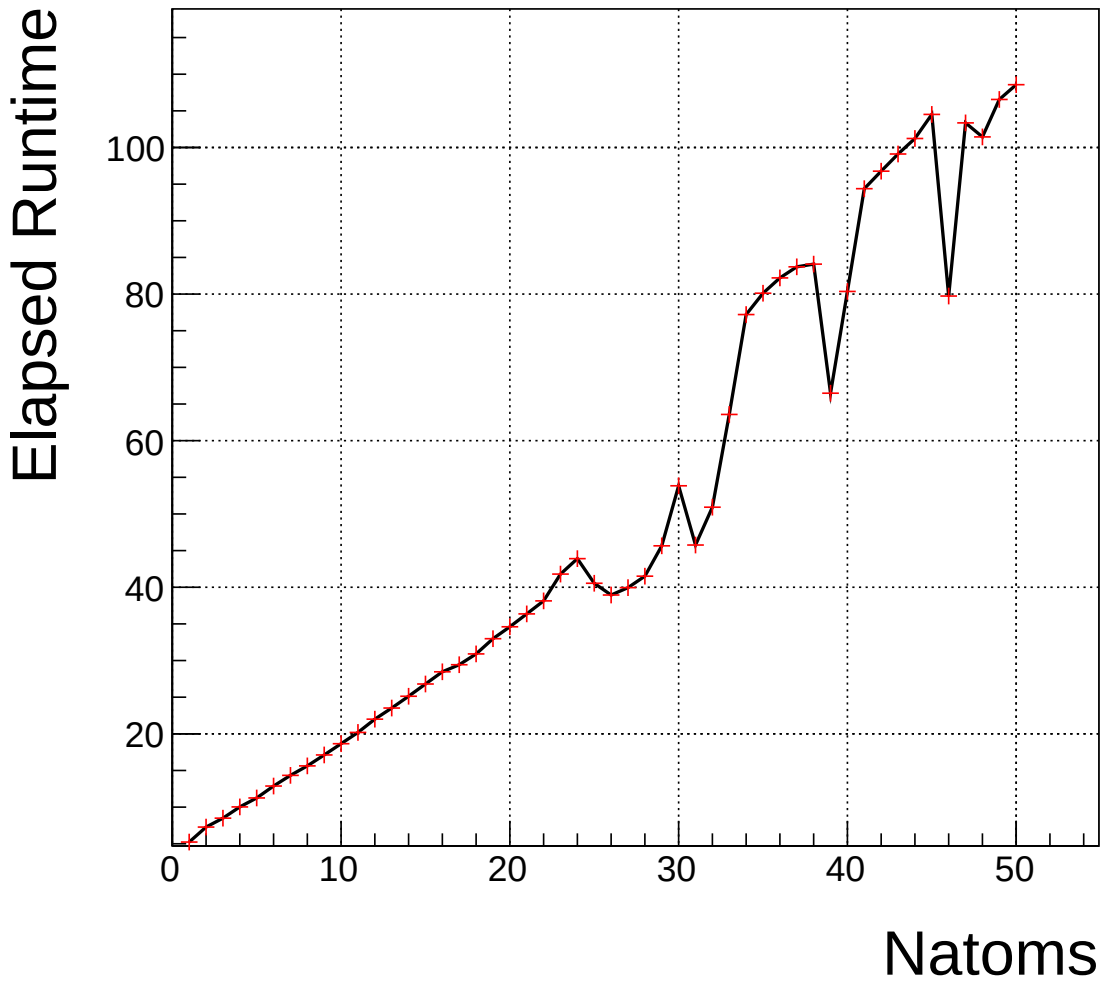

Figure 6: Runtime (in seconds) as a function of number of atoms

In practice a molecular dynamics simulation encompasses billions of atoms or more, here in this assignment the simulation is limited to a disappointing-maximum of fifty atoms. As illustrated by figure 6 each individual simulation run takes longer than 60 seconds (and more). Meaning I had to wait an amount of time, that is upwards of fifteen minutes after a simulation of 30 atoms, with only 5000 time steps. In practice I would like to be able to simulate a system with a billion time steps - but I am limited here to 5000! Lol.

My simulation even with localized interaction force calculations, meaning I looked for the nearest neighbors within a small region around my particles did not help. These results reflect the grid based system approach to finding interaction forces of only the nearest neighbors, and still my simulation was very slow. Its easy to blame the programming language I used. But I believe it may be my own programming inexperience that may have led to inefficiencies.

I realize now that after looking at Figures 4 and 5 for a temperature=10 and alpha=1, the energy should be near 10 which is the case for simulations where natoms is between 1 and 10. Whenever my stem has more than 10 atoms the energy starts increasing. This tells me my algorithm for calculating the forces and thereby the velocity may be askew. **I would like to walk you through my code to pinpoint where my algorithm may be incorrect - at some point in the future.** I will also be re-implementing this code in C/C++ in the near future.

For the time being also simulated a thermostat system with T=0.75 and these conditions:

- α =1
- temperature(T)=0.75
- mass(m)=1
- Boltzmann constant(k_b)=1
- time step (dt)=0.001
- total number of time steps=5000

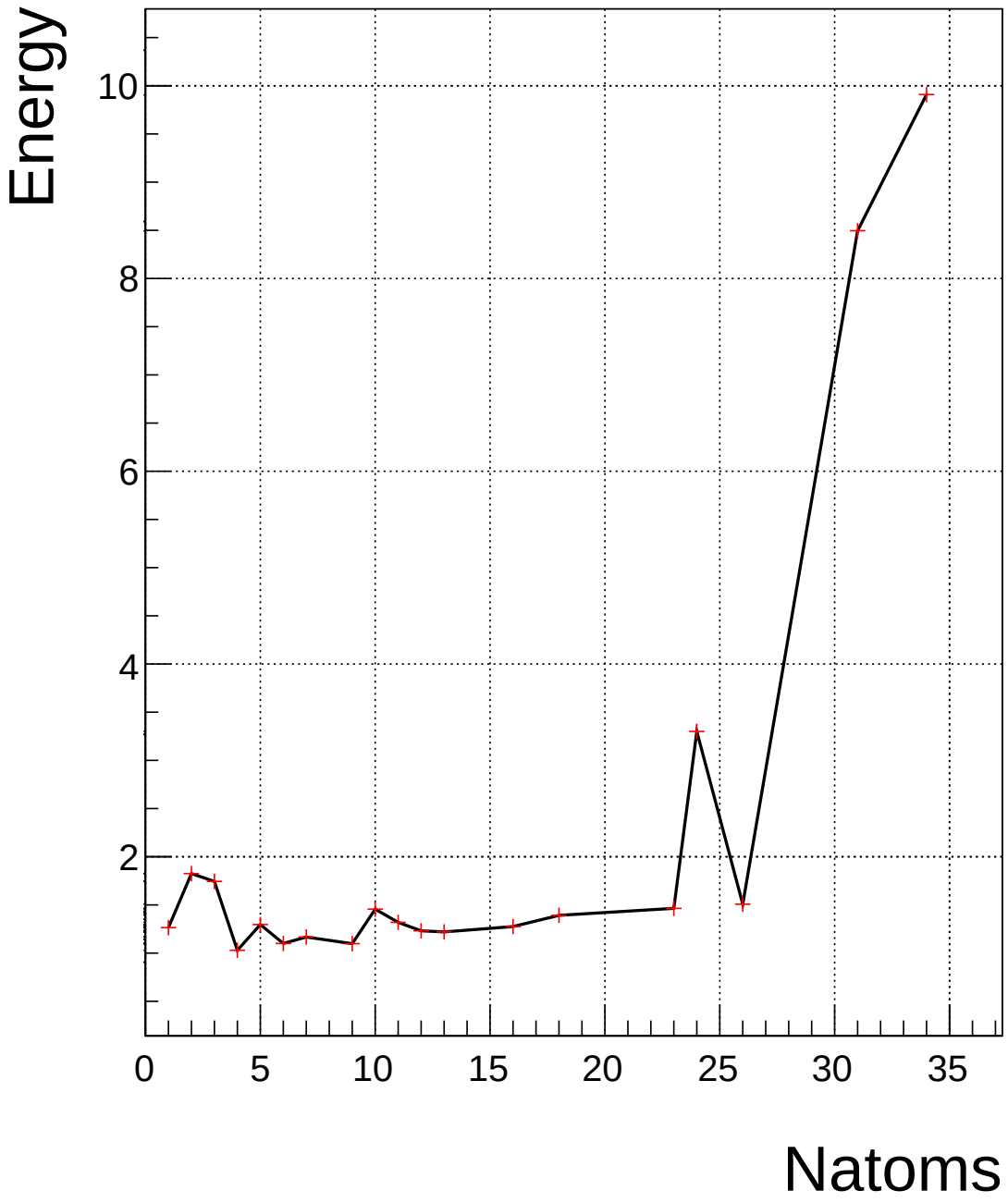

Figure 7: Average box system energy as a function of number of atoms

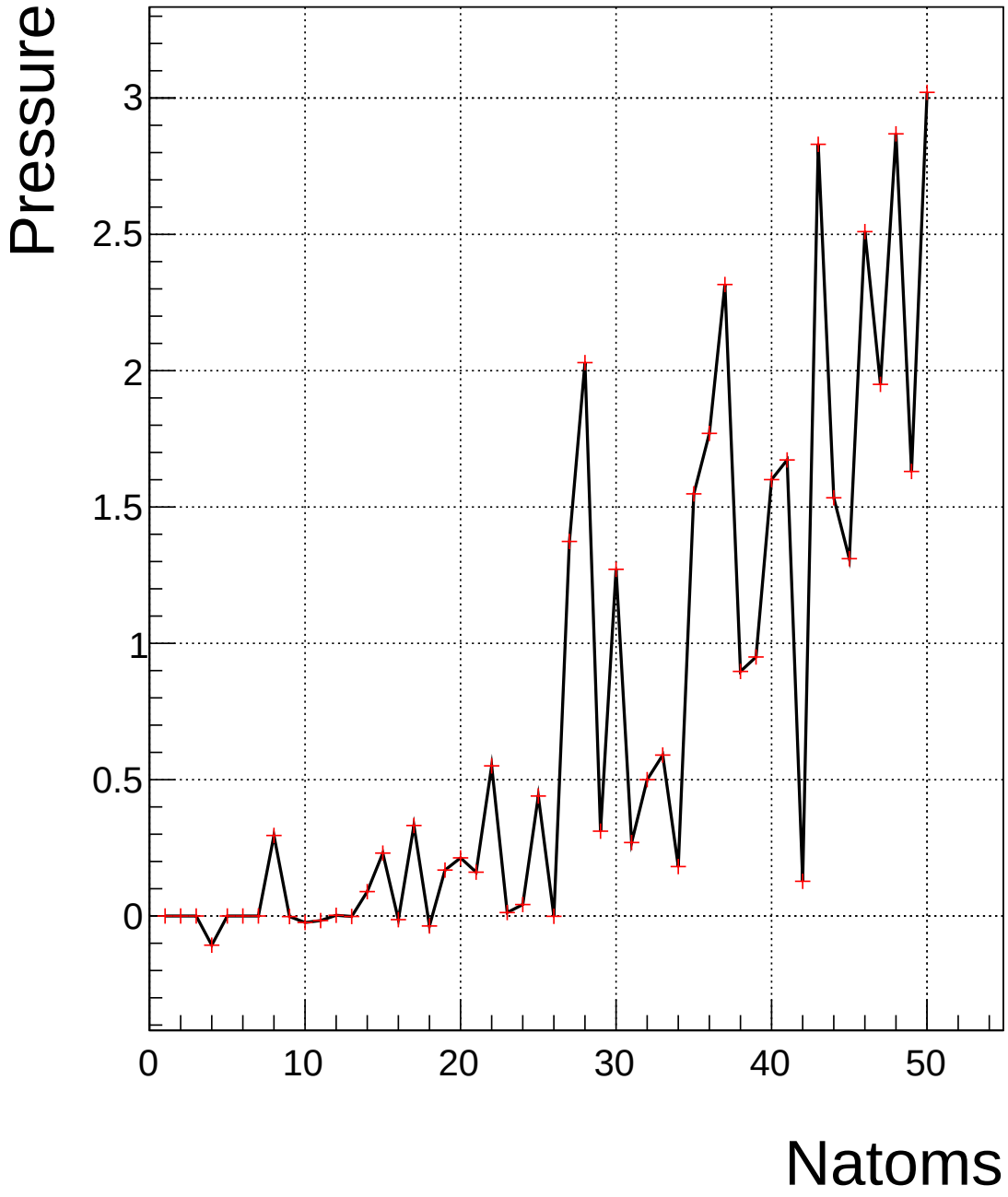

Figure 8: Average box system pressure as a function of number of atoms

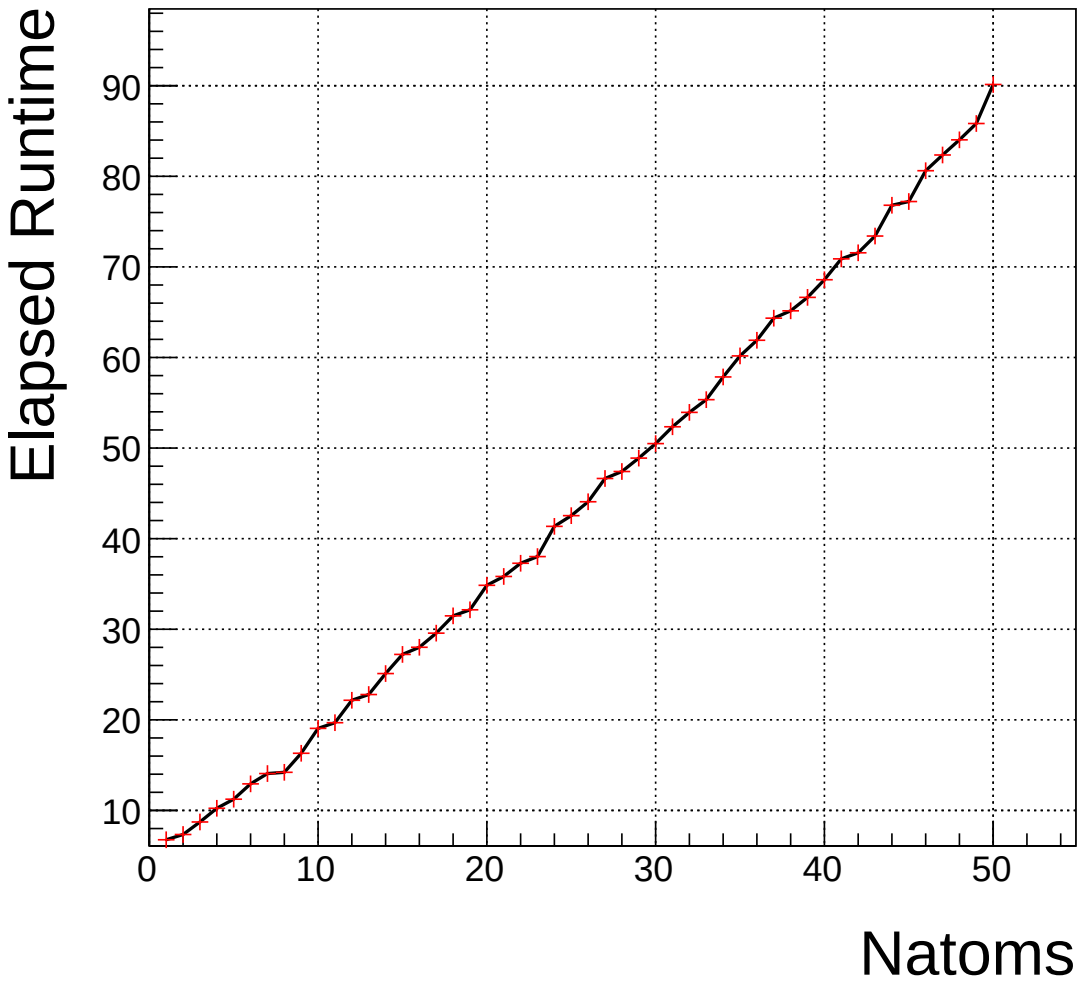

Figure 9: Runtime (in seconds) as a function of number of atoms