MD-Assignment 2

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1 Assignment

Implement the force-field equations derived in class to obtain a box of particles bouncing off walls and off each other. We can think of the normalized x-direction and y-direction as (ξ,η). Determining newton second law motion equations can be seen in the following steps:

1.1 Basics

How do we get a force from potentials? Simple, we take the negative derivative (with respect to a spatial axis) of a vector potential, or we can take the negative gradient of a scalar potential. We show the forces on a particle in a box from this basic definition, equation (2).

Here's a look at the gradient.

$$-\nabla = \begin{bmatrix} -\frac{\partial}{\partial \xi} \\ -\frac{\partial}{\partial \eta} \end{bmatrix} \tag{1}$$

We should internalize this definition of force, equation (2). It is enough to analytically determine the force then plug this new definition into our working code.

$$\vec{F} = -\nabla \cdot \phi\left(\xi, \eta\right) \tag{2}$$

This document will show the exact force derived analytically for expressions of forces we use in our simulation code.

1.2 System Potentials

Let us give an overview of the potential energy within our particles in a box framework.

1.2.1 Wall Potentials:

We first introduce the potential energy of all four sides of our confined box. Let it be known that ξ and η represent the conventional x-y axis respectively.

Potential energy of the **left**-side wall.

$$\phi\left(\xi\right) = \left[\left(\frac{1}{\xi}\right)^{12} - 2\left(\frac{1}{\xi}\right)^{6}\right] \tag{3}$$

Potential energy of the **right**-side wall.

$$\phi\left(l - \xi\right) = \left[\left(\frac{1}{l - \xi}\right)^{12} - 2\left(\frac{1}{l - \xi}\right)^{6}\right] \tag{4}$$

Potential energy of the **bottom**-side wall.

$$\phi\left(\eta\right) = \left[\left(\frac{1}{\eta}\right)^{12} - 2\left(\frac{1}{\eta}\right)^{6}\right] \tag{5}$$

Potential energy of the **top**-side wall.

$$\phi\left(l-\eta\right)=\left[\left(\frac{1}{l-\eta}\right)^{12}-2\left(\frac{1}{l-\eta}\right)^{6}\right] \tag{6}$$

The summed result of all the potentials above, provide the expression for total energy from the wall. We use all four sides to compose the total scalar value of the wall contribution to a particles potential energy.

$$\phi\left(\xi,\eta\right)=\phi\left(\xi\right)+\phi\left(l-\xi\right)+\phi\left(\eta\right)+\phi\left(l-\eta\right) \tag{7}$$

1.2.2 Lennard-Jones Potential

Each and every particle within our particle in a box model, experiences a reactionary force or potential energy contribution from neighboring particles. Later we will look at neighbors restricted to certain range around a particle, but for this assignment we look at the exhaustive calculation between all particles.

$$\begin{aligned}
|\vec{\eta}_i-\vec{\eta}_j| &= \theta_{i,j}\left(\xi_i,\eta_i,\xi_j,\eta_j\right)=\sqrt{(\xi_i-\xi_j)^2+(\eta_i-\eta_j)^2}\\
U_{LJ}\left(\theta_{i,j}\right) &= \left\{\left(\frac{1}{|\vec{\eta}_i-\vec{\eta}_j|}\right)^{12}-2\left(\frac{1}{|\vec{\eta}_i-\vec{\eta}_j|}\right)^{6}\right\}\\
&= \boxed{\left\{\left(\frac{1}{\sqrt{(\xi_i-\xi_j)^2+(\eta_i-\eta_j)^2}}\right)^{12}-2\left(\frac{1}{\sqrt{(\xi_i-\xi_j)^2+(\eta_i-\eta_j)^2}}\right)^{6}\right\}}
\end{aligned}$$

In a exhaustive calculation of all particle energies, the routine for calculating energies will look like so:

- particle 1: [11, 12, 13, 14]
- particle 2: [21, 22, 23, 24]
- particle 3: [31, 32, 33, 34]
- particle 4: [41, 42, 43, 44]

Already we begin to see for a four particle system, the lennard jones potential can be represented within a matrix. Let me clarify that the numbers 11, 12, 13, and so forth, mean the energy/force on particle 1 from particle 1 (1 onto 1). **Likewise '12' means the force/energy on particle 1 from particle 2**. Notice that particle energy of particle 1 onto 1 (11), is zero, because a particle cannot feel interaction energy contributions from itself. So essential whenever indices, or the i^{th} and j^{th} components are matching we define this in code to be zero.

```python
import numpy as np

u_lj_mat=np.zeros((natoms,natoms))

for n_dt in range(0,ndtsteps):
    for time_step in range(0,nsteps):
        for i in range(0,natoms):
            for j in range(i,natoms):
                if i==j:
                    r[i][j]=0
                    u_lj_mat[i][j]=0
                else:
                    u_lj_mat[i][j]=lennard_jones_potential(r[i][j])
                    u_lj_mat[j][i]=u_lj_mat[i][j]
```

2 Forces:

2.1 Wall Forces

To model the motion of a particle in a box, we need to compute the force vectors.

$$\begin{aligned}
\vec{F_\xi} &= -\frac{\partial\left[\phi\left(\xi\right)+\phi\left(l-\xi\right)+\phi\left(\eta\right)+\phi\left(l-\eta\right)\right]}{\partial\xi} \\
&= -\left[\frac{\partial(\phi\left(\xi\right))}{\partial\xi}+\frac{\partial[\phi\left(l-\xi\right)]}{\partial\xi}+\frac{\partial\left[\phi\left(\eta\right)\right]}{\partial\xi}+\frac{\partial[\phi\left(l-\eta\right)]}{\partial\xi}\right] \\
&= F_\xi\left(\xi\right)+F_\xi\left(L-\xi\right)+F_\xi\left(\eta\right)+F_\xi\left(L-\eta\right)
\end{aligned}$$

$$\begin{aligned}
\vec{F_\eta} &= -\frac{\partial\left[\phi\left(\xi\right)+\phi\left(l-\xi\right)+\phi\left(\eta\right)+\phi\left(l-\eta\right)\right]}{\partial\eta} \\
&= -\left[\frac{\partial(\phi\left(\xi\right))}{\partial\eta}+\frac{\partial[\phi\left(l-\xi\right)]}{\partial\eta}+\frac{\partial\left[\phi\left(\eta\right)\right]}{\partial\eta}+\frac{\partial[\phi\left(l-\eta\right)]}{\partial\eta}\right] \\
&= F_\eta\left(\xi\right)+F_\eta\left(L-\xi\right)+F_\eta\left(\eta\right)+F_\eta\left(L-\eta\right)
\end{aligned}$$

I'll show the process of deriving the horizontal, x-ξ axis forces. All that is needed to determine the analytical boundary force is to take the first derivative of the potential energy expression, equation (7). We will show the details of finding the vector components for force in the horizontal direction, which is the ξ direction by our notation. So we make all derivative with respect to ξ.

2.1.1 ξ Force

Force of the **left**-side wall (ξ-direction)

$$\begin{aligned}
F_\xi(\xi) &= -\frac{\partial[\phi\left(\xi\right)]}{\partial\xi} \\
&= -\frac{\partial}{\partial\xi}\left[\left(\frac{1}{\xi}\right)^{12}-2\left(\frac{1}{\xi}\right)^{6}\right] \\
&= -\left[-12\left(\frac{1}{\xi}\right)^{13}\frac{\partial(\xi)}{\partial\xi}+12\left(\frac{1}{\xi}\right)^{7}\frac{\partial(\xi)}{\partial\xi}\right] \\
&= \boxed{12\left[\left(\frac{1}{\xi}\right)^{13}-\left(\frac{1}{\xi}\right)^{7}\right]}
\end{aligned}$$

Force of the **right**-side wall (ξ-direction)

$$
\begin{aligned}
F_\xi(L-\xi) &= -\frac{\partial[\phi\,(l-\xi)]}{\partial \xi} \\
&= -\frac{\partial}{\partial \xi}\left[\left(\frac{1}{l-\xi}\right)^{12} - 2\left(\frac{1}{l-\xi}\right)^{6}\right] \\
&= -\left[-12\left(\frac{1}{l-\xi}\right)^{13}\frac{\partial(l-\xi)}{\partial \xi} + 12\left(\frac{1}{l-\xi}\right)^{7}\frac{\partial(l-\xi)}{\partial \xi}\right] \\
&= -\left[12\left(\frac{1}{l-\xi}\right)^{13} - 12\left(\frac{1}{l-\xi}\right)^{7}\right] \\
&= \boxed{-12\left[\left(\frac{1}{l-\xi}\right)^{13} - \left(\frac{1}{l-\xi}\right)^{7}\right]}
\end{aligned}
$$

Force of the **bottom**-side wall (ξ-direction)

$$
\begin{aligned}
F_\xi &= -\frac{\partial\left[\phi\,(\eta)\right]}{\partial \xi} \\
&= \boxed{0}
\end{aligned}
$$

Force of the **top**-side wall (ξ-direction)

$$
\begin{aligned}
F_\xi &= -\frac{\partial[\phi\,(l-\eta)]}{\partial \xi} \\
&= \boxed{0}
\end{aligned}
$$

Complete expression of horizontal force in the ξ direction.

$$
\begin{aligned}
F_\xi &= \frac{\partial\left\{\phi\,(\xi)\right\}}{\partial \xi} + \frac{\partial\left\{\phi\,(l-\xi)\right\}}{\partial \xi} + \cancelto{0}{\frac{\partial\left\{\phi\,(\eta)\right\}}{\partial \xi}} + \cancelto{0}{\frac{\partial\left\{\phi\,(l-\eta)\right\}}{\partial \xi}} \\
&= \boxed{12\left[\left(\frac{1}{\xi}\right)^{13} - \left(\frac{1}{\xi}\right)^{7}\right] + -12\left[\left(\frac{1}{l-\xi}\right)^{13} - \left(\frac{1}{l-\xi}\right)^{7}\right] + 0 + 0}
\end{aligned}
$$

2.1.2 η Force

$$
\begin{aligned}
F_\eta &= \cancelto{0}{\frac{\partial\left\{\phi\,(\xi)\right\}}{\partial \eta}} + \cancelto{0}{\frac{\partial\left\{\phi\,(l-\xi)\right\}}{\partial \eta}} + \frac{\partial\left\{\phi\,(\eta)\right\}}{\partial \eta} + \frac{\partial\left\{\phi\,(l-\eta)\right\}}{\partial \eta} \\
&= \boxed{0 + 0 + 12\left[\left(\frac{1}{\eta}\right)^{13} - \left(\frac{1}{\eta}\right)^{7}\right] + -12\left[\left(\frac{1}{l-\eta}\right)^{13} - \left(\frac{1}{l-\eta}\right)^{7}\right]}
\end{aligned}
$$

2.1.3 Wall Force Code

```
def wall_force(xi,nu):
    fx_left_boundary    = 12*((1/xi)**13-(1/xi)**7)
    fx_right_boundary   = -12*((1/(l-xi))**13-(1/(l-xi))**7)
    fx                  = fx_left_boundary+fx_right_boundary

    fy_bottom_boundary  = 12*((1/nu)**13-(1/nu)**7)
    fy_top_boundary     = -12*((1/(l-nu))**13-(1/(l-nu))**7)
    fy                  = fy_bottom_boundary+fy_top_boundary
    return fx,fy
```

2.2 Interaction Forces

Normalization constants

$$x = x_0\xi$$
$$y = y_0\eta$$
$$r = r_0\Gamma$$

$$r = r_0\gamma = \sqrt{(x_0\xi)^2 + (y_0\eta)^2}$$

deriving normalized interaction force equation

$$\vec{f}_{i,j} = -\nabla U_{LJ} \tag{8}$$

$$= -\begin{bmatrix} \frac{\partial}{\partial \xi} \\ \frac{\partial}{\partial \eta} \end{bmatrix} \cdot U_{LJ}(\vec{r}_{i,j}) \tag{9}$$

$$= \frac{E_0 12}{r_0}\left[\left(\frac{r_0}{|\vec{r}_i - \vec{r}_j|}\right)^{13} - \left(\frac{r_0}{|\vec{r}_i - \vec{r}_j|}\right)^{7}\right]\begin{bmatrix} \frac{\partial|\vec{r}_i - \vec{r}_j|}{\partial x} \\ \frac{\partial|\vec{r}_i - \vec{r}_j|}{\partial y} \end{bmatrix} \tag{10}$$

$$= \frac{E_0 12}{r_0}\left[\left(\frac{r_0}{r_0|\vec{\Gamma}_i - \vec{\Gamma}_j|}\right)^{13} - \left(\frac{r_0}{r_0|\vec{\Gamma}_i - \vec{\Gamma}_j|}\right)^{7}\right] \cdot \frac{1}{(|\vec{r}_i - \vec{r}_j|)} \cdot \begin{bmatrix} x_i - x_j \\ y_i - y_j \end{bmatrix} \tag{11}$$

$$= \frac{E_0 12}{r_0}\left[\left(\frac{1}{|\vec{\Gamma}_i - \vec{\Gamma}_j|}\right)^{13} - \left(\frac{1}{|\vec{\Gamma}_i - \vec{\Gamma}_j|}\right)^{7}\right] \cdot \frac{1}{r_0\left(|\vec{\Gamma}_i - \vec{\Gamma}_j|\right)} \cdot \begin{bmatrix} x_0(\xi_i - \xi_j) \\ y_0(\eta_i - \eta_j) \end{bmatrix} \tag{12}$$

$$\text{if } x_0 = 1 \text{ and } y_0 = 1 \text{ then } r_0 = \sqrt{2}. \tag{13}$$

$$\cancelto{1}{\left[\frac{m_0 x_0^2}{t_0^2} \cdot \frac{r_0}{E_0}\right]} \frac{\mu d^2(\xi)}{dt^2} = 12\left[\left(\frac{1}{|\vec{\Gamma}_i - \vec{\Gamma}_j|}\right)^{13} - \left(\frac{1}{|\vec{\Gamma}_i - \vec{\Gamma}_j|}\right)^{7}\right] \cdot \cancelto{\frac{1}{\sqrt{2}}}{\frac{x_0}{r_0}} \cdot \frac{\xi_i - \xi_j}{\left(|\vec{\Gamma}_i - \vec{\Gamma}_j|\right)} \tag{14}$$

$$\frac{\mu d^2(\xi)}{dt^2} = 12\left[\left(\frac{1}{|\vec{\Gamma}_i - \vec{\Gamma}_j|}\right)^{13} - \left(\frac{1}{|\vec{\Gamma}_i - \vec{\Gamma}_j|}\right)^{7}\right] \cdot \frac{1}{\sqrt{2}} \cdot \frac{\xi_i - \xi_j}{\left(|\vec{\Gamma}_i - \vec{\Gamma}_j|\right)} \tag{15}$$

Equation 15 represents the interaction force in the ξ direction. A similar equation must me written for the interaction force in the η direction.

2.3 Interaction force code

Here's a look at the pythonic defined interaction force code.

```
def lennard_jones_force(x_i,x_j,eta_i,eta_j):
    gamma       = np.sqrt( (x_i-x_j)**2 + (eta_i-eta_j)**2) #magnitude of separation between vectors
    fx          = (1/gamma**13 + 1/gamma**7)*((x_i-x_j)/gamma)*(12/np.sqrt(2))
    fy          = (1/gamma**13 + 1/gamma**7)*((eta_i-eta_j)/gamma)*(12/np.sqrt(2))
    return fx,fy
```

Then this function is used like so..

```
'''============================
    dt Loop
    ==========================='''
for n_dt in range(0,f.ndt):
        '''============================
```

```
            time Loop
            ==========================='''
        for n_time in range(0,f.nstep):
            for i in range(0,f.natom): #ith particle
                '''=========================================
                    Lennard-Jones Potential Calculation
                    ========================================='''
                for j in range(i,f.natom): #jth particle
                    r[i][j]=((f.x[i]-f.x[j])**2+(f.y[i]-f.y[j])**2)**1/2.
                    r[j][i]=r[i][j]
                    if i==j:
                        r[i][j]=0
                        u_jones_matrix[i][j]=0
                        f_jones_matrix[i][j]=0
                    else:
                        u_jones_matrix[i][j]=lennard_jones_potential(r[i][j])
                        u_jones_matrix[j][i]=u_jones_matrix[i][j]
                        f_jones_matrix[i][j]=lennard_jones_force(x[i],x[j],y[i],y[j])
                        f_jones_matrix[j][i]=-f_jones_matrix[i][j]
                '''=========================================
                    Verlet Motion Algorithm
                    ========================================='''
                f.t[0]=f.dt[0]*n_time
                f.ux[i]=f.vx[i]+f.dt[0]*f.fx[i]/(2*f.m[0])
                f.uy[i]=f.vy[i]+f.dt[0]*f.fy[i]/(2*f.m[0])
                f.x[i]=f.x[i]+f.ux[i]*f.dt[0]
                f.y[i]=f.y[i]+f.uy[i]*f.dt[0]

                f_wall_x,f_wall_y=wall_force(f.x[i],f.y[i])
                f_lj_x=np.sum(f_jones_matrix_x[i])
                f_lj_y=np.sum(f_jones_matrix_y[i])
                f.fx[i]=f_wall_x+f_lj_x
                f.fy[i]=f_wall_y+f_lj_y

                f.vx[i]=f.ux[i]+f.dt[0]*f.fx[i]/(2*f.m[0])
                f.vy[i]=f.uy[i]+f.dt[0]*f.fy[i]/(2*f.m[0])
```

Let me explain the outer most for loop ('dt loop') is meant for changing the value of the time step (dt); while, the 'time loop' is meant for incriminating the time step. At a particular time step value, I select an i'th particle (in the for i loop) and calculate the interaction with the for j loop.

3 Tasks

- Things to do:
  1. Calculate and display a trace of the particles motion as it is making a reasonable number of collisions with each of the walls.
  2. Calculate the potential and kinetic energies as a function of time (KE(t), PE_Wall(t), PE_LJ(t))
  3. Calculate the total energies as a function of time (KE(t)+PE_Wall(t)+PE_LJ(t))
  4. Show (Total Energy vs. dt)

4 Motion

An example of a single particle in a box only interacting with the walls Figure 1 and 2. Particle trace for single and multiple particles as seen in Figure 1 and Figure 2. These particles illustrate tracks for initial velocities of vx_0=1 and vx_y=2.

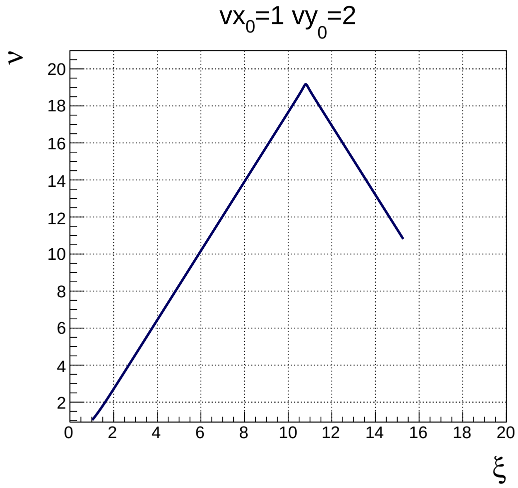

Figure 1: Single particles

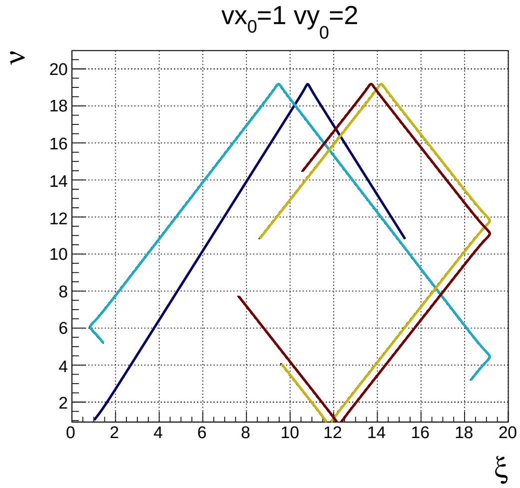

Figure 2: Multiple particles

4.1 Spatial Energy Plots

Here's a look at various energies (potential, kinetic) for both full step velocity (V^n) and half step (U^n) velocities as a function of position. Note the wall potential asymptotically increases as the particle approaches the wall boundary. Additionally, the Lennard Jones potential seems to shoot to infinity due to the occurrence of knocking into another particle.

However we see the Lennard Jones potential stays at equilibrium when we simulate a single particle in a box. Due to the fact that this single particle does not interact with any auxiliary particles, the Lennard Jones has no opportunities to change - as seen in figure 3. However, Lennard Jones has opportunities to deviate from equilibrium in the occurrence that the particle approaches another particle. We see that Particle 2 (of the 20 atom box systemå) comes close to other particles and that the Lennard Jones potential approaches infinity, Figure 4.

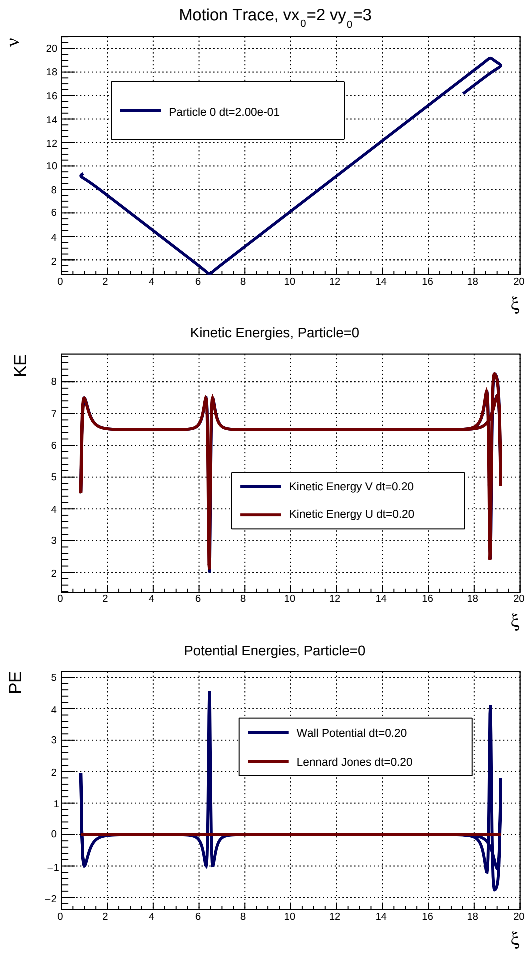

Figure 3: 1 atom in a box

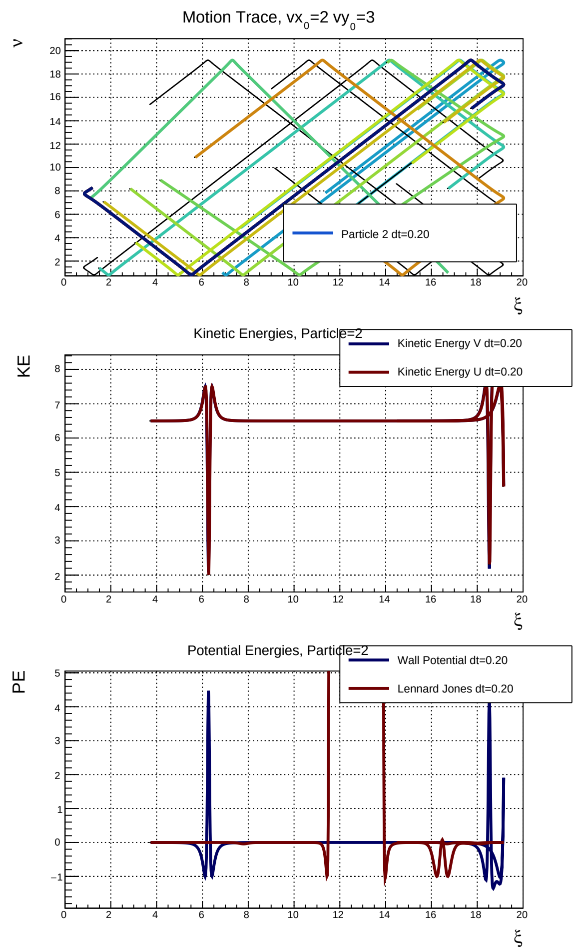

Figure 4: 20 atoms in a box

5 Force and Energy Analysis

Plenty of computational complications arise from normalization inaccuracies, let alone failing to normalize at all. Normalizing an equation so a computer may compute an equation is essential for simulation. In the previous plots, forces, potentials, and kinetic energies were computed with normalized values.

A look at the x (ξ) and y (η) wall-boundary forces with respect to time.

6 Energy

6.1 Average total energy and time

For a single particle there shouldn't be any lennard jone contributions, since there are no auxiliary partices to interact with. This plot, Figure 5, demonstrates kinetic energy hovering around 6.5 (normalized units). This makes sense because $KE = 1/2m(v_x^2 + v_y^2)$.

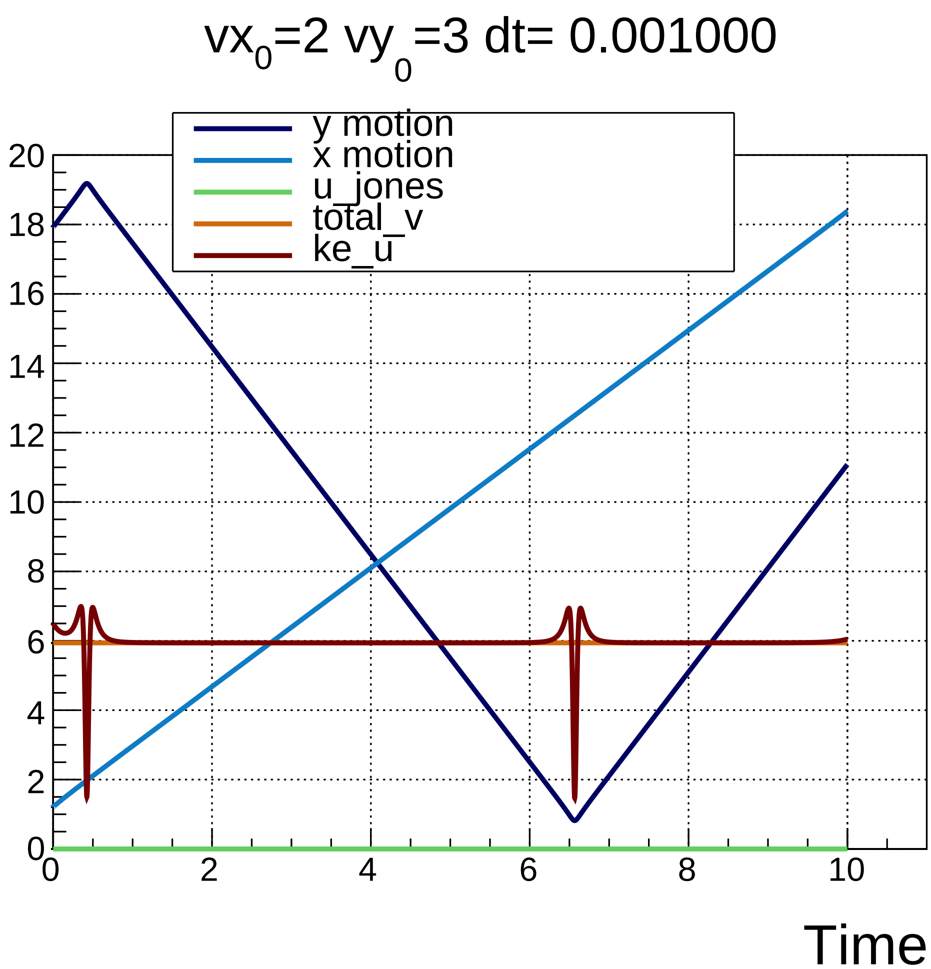

Figure 5: 1 particle in a box

When we introduce more particles into the picture (figuratively speaking) and allocate five particles in a box. There is a compelling chance there will be a collision which will spike the lennard jones potential to infinity. It is clear that, whenever there's an interaction between particles the lennard jones potential shoots to infinity, in Figure 6.

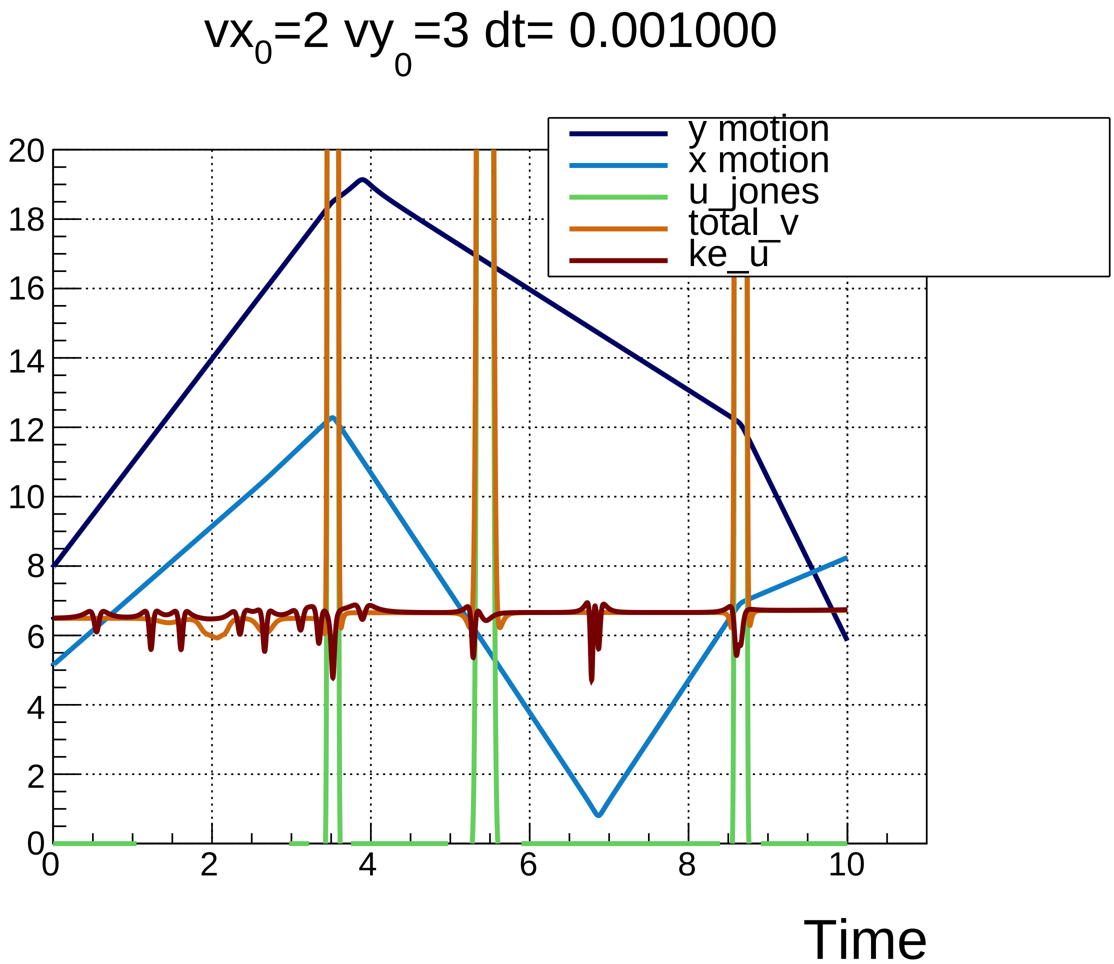

Figure 6: 5 particles in a box

The time step needs to be very small (dt≈0.001) to prevent overall energy ('total_v') from becoming unstable. Despite normalization this energy increases the kinetic energy beyond repair when dt is beyond 0.005 (Figure 8).
The 'y motion' and 'x motion' (In Figure 5 and 6) represent the trajectories of a particle (the first particle in the box) in the y (η) and x (ξ) direction.

6.2 Average energy and time step (dt)

Here's a look at the average kinetic and total energy (sum of of kinetic, wall potential, and lennard jones potential) for a box with one particle. Here's a look at the average kinetic and total energy (sum of of kinetic, wall potential, and lennard jones potential) for a box with five particles.

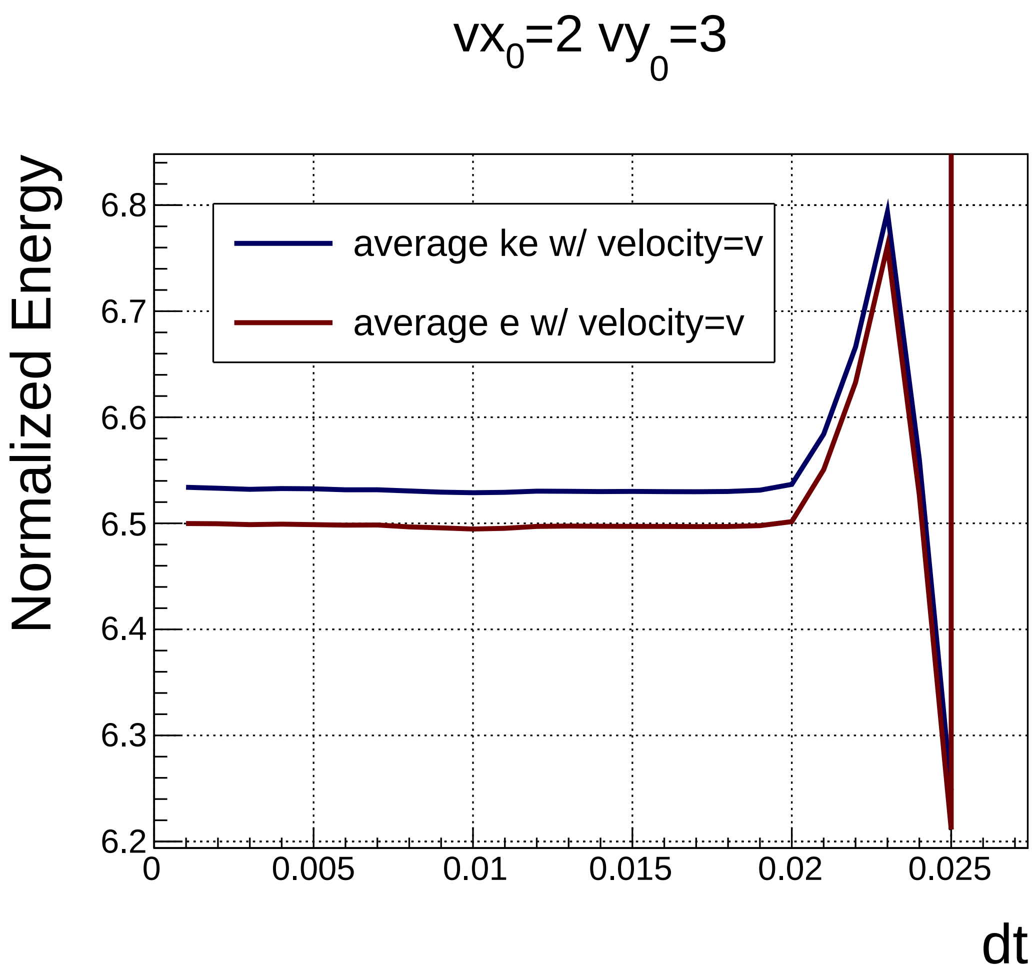

Figure 7: Energy vs dt (single particle)

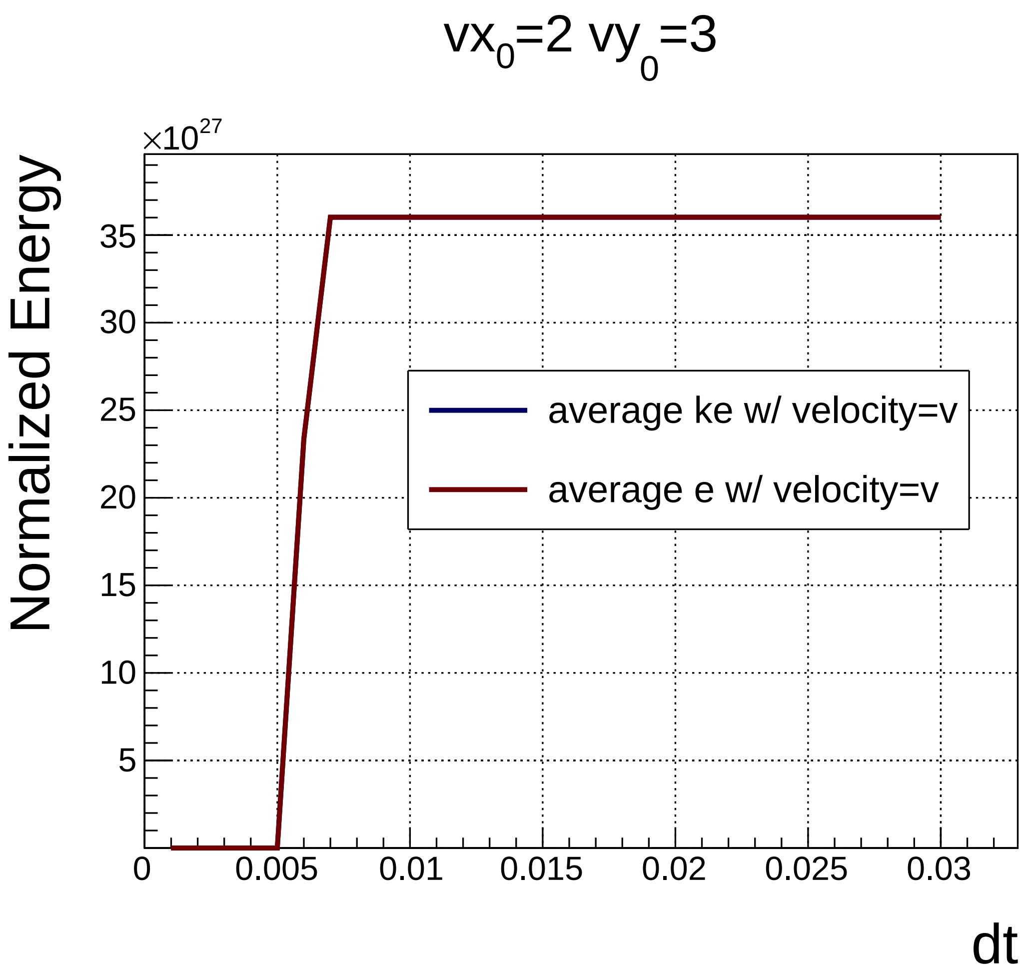

Figure 8: Energy vs dt (5 particles)