Ex10_MarkovianLangevinDynamics

February 2, 2021

1 Exercise 10 :

2 Markovian Langevin Dynamics

- Léa Beaules
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[154]:
```
%matplotlib inline
import matplotlib.pyplot as plt
from matplotlib import animation, rc
from IPython.display import HTML
import random
import copy
import numpy as np
import scipy as scy
from tqdm.notebook import trange, tqdm
import time
from scipy.stats import maxwell

#used for the video
import subprocess
import glob
import os
```

2.1 Introduction

We simulate 50 particles in a box (5nmx5nm) with periodic boundary condictions. The particules interact with each other via the lLennard-Jones potential and the velocities and positions are calculated with the Velocity Verlet integrator and van der Waals forces. Because this type of simulations causes the artificial generation of excess heat we add in the simulation the Berendsen thermostat, which keeps the total energy of the system constant instead of artificially increasing. In the last exercice we calculated the autocorrelation function as well as the Stokes friction coefficient.

The specificity of this simulation is that out of the 50 particles, two of them (1st and 50th) are bound to each other in such a way that their distance in constant over time. They will start with an initial velocity = 0, and at each time step we cancel out the contibution of the force along their connecting vector (by appliying a "Constraint force").

We will finally calculate the Free energy of thoses two particles and compare it the their potential

energy. And similarly to the last exercice we calculate the constraint force autocorrelation function as well as the Stokes friction coefficient. And compare them to previous results.

2.2 Task I: Implementation of Markovian Langevin dynamics

LE integrator : $\vec{v_{k+1}} = \vec{v_k} - \frac{1}{m}(\frac{d\vec{U_k}}{d\vec{x_k}}\Delta t + \vec{v_k}\Gamma\Delta t - \sqrt{2\Gamma k_b T \Delta t}R_k)$

Knowing that for this simulation our potential U is to be equal everywhere, we get : $\frac{d\vec{U_k}}{d\vec{x_k}} = 0$, therefor for simplification we won't have this term in our function and we will implement :

$$\vec{v_{k+1}} = \vec{v_k} - \frac{N_a}{m}(\vec{v_k}\Gamma\Delta t - \sqrt{2 * 10^3\Gamma k_b T \Delta t}R_k)$$

Constant troughout the simulation : * Δt : time step length * Γ : friction constant * k_b : Bolzmann connstant * T : Temperature

Changing at each step k : * R_k : is a normally distributed stochastic process * v_k : velocity

[155]:
```
def LE_integrator (v_k_vec):
    v_k_x = v_k_vec[0]
    v_k_y = v_k_vec[1]

    # Simulating a kick on the particle with random direction
    R_k = np.random.standard_normal(1)
    R_k_angle = np.random.uniform(0,2*np.pi)
    R_kx = np.sin(R_k_angle)*R_k
    R_ky = np.cos(R_k_angle)*R_k

    v_k1_x = v_k_x - Na/mass * (v_k_x*Gamma*Dlt_t_s - np.
↪sqrt(2*Gamma*k_b*Temp*Dlt_t_s) * R_kx)
    v_k1_y = v_k_y - Na/mass * (v_k_y*Gamma*Dlt_t_s - np.
↪sqrt(2*Gamma*k_b*Temp*Dlt_t_s) * R_ky)

    #print(- Na/mass * (v_k_y*Gamma*Dlt_t_s - np.sqrt(2*Gamma*k_b*Temp*Dlt_t_s)␣
↪* R_ky))

    return [v_k1_x, v_k1_y]
```

2.3 Task II : LE Simulation

Simulation of 50 particules in a 5x5nm box (with PBC), with 2 having a constant distance between each other.
The interparticle interaction is modeled as a Lennard-Jones potential.
The Velocity Verlet integrator is used to calculate the motion of the particles. The following constant are used :

[156]:
```
box = (5,5)#nm²

#1.000.000 total time steps in the simulation
```

```
steps = 1000000

#Number of particles in the box
Particule_Nbr = 1
mass = 18 #g/mol

#Time step (2*e-6 in nm)
Dlt_t = 2e-6 #ns = 1fs
Dlt_t_s = 2e-15#in second

#Fricction constant
Gamma = 2.1e-13 #Kg/s -13

k_b_mol = 8.314462 #J K^(-1).mol^(-1)
k_b = 1.380649e-23 #J.K-1

Na = 6.02214086e23 #mol-1
Temp = 293.15 #K


time_list_plot = np.linspace(0,steps,steps)[0:-1]
```

Position

The potential U is assumed to be constant so there is no acceleration on our particle.

$x_{k+1} = x_k + v_k \Delta t$

[157]:
```
def position (x_k, v_k, Dlt_t):
    x_k1 = x_k + v_k*Dlt_t
    return x_k1
```

[158]:
```
def get_vect_r(x,y, x2, y2):
    x_list =[]
    x_list += [x2 - x]
    x_list += [x2 - x + box[0]]
    x_list += [x2 - x - box[0]]
    x_part = min(x_list, key=abs)

    y_list =[]
    y_list += [y2 - y]
    y_list += [y2 - y + box[1]]
    y_list += [y2 - y - box[1]]
    y_part = min(y_list, key=abs)

    r = [x_part, y_part]

    return r
```

Velocity

Here :

$v_{k+1} = v_k + \frac{1}{2}(a_k + a_{k+1})\Delta t$

is not used anymore but the LE integrator is used instead to calculate the velocity

Kinetic energy

$E_{kin} = \frac{1}{2}m < v^2 >$

[159]:
```
def Kinetic(Data_traj_list, time_t):
    K_list = []
    for p_ind in range (Particule_Nbr):
        p_vx = Data_traj_list[2,time_t]
        p_vy = Data_traj_list[3,time_t]
        v = np.sqrt(p_vx**2 + p_vy**2)
        K_list += [v**2]
    K = (1/2)*mass*np.mean(K_list)
    K = K * 10**(-3) #unit convertion into J/mol

    return K
```

Plot the simulation

[160]:
```
def plot(t):
    for parti in range (Particule_Nbr):
        data_traj = Data_traj_list[parti]
        #Particule = Particules_list[parti]
        c = 'indigo'
        if parti ==0 or parti == 49:
            c = 'cadetblue'

        plt.plot(data_traj[0,t],data_traj[1,t], marker='.', markersize='10', ␣
↪linestyle = '-', color=c)
```

[161]:
```
def plot(data_traj, name):

    x = data_traj[0,:]
    y = data_traj[1,:]


    c = 'indigo'
    plt.plot(x,y, marker='.', markersize='3',  linestyle = 'None', color = c)
    plt.plot(data_traj[0,0],data_traj[1,0], marker='.', markersize='7', ␣
↪linestyle = '-', alpha=1, color = 'cadetblue')

    plt.xlabel('position x')
    plt.ylabel('position y')
    plt.xlim(0,5)
    plt.ylim(0,5)
```

```
    Titles_graph1 = name + ' Simulation with ' + str(steps) + 'steps'
    plt.title(Titles_graph1)
    plt.show()

    return (x,y)
```

Initialise simulation

The particle is placed at a random position in the box, and has an initial velocity coresponding to the thermal velocity for T=293.15 K ($v_0 = \sqrt{\frac{k_b T}{m}} = 11.636 m.s^{-1}$) and starts with a random direction.

We store the trajectory and velocity for each step of the siimulation in the array : Data_traj_list. First indice : * 0 : x position in x * 1 : y position in y * 2 : vx velocity along x * 3 : vy velocity along y

Second indice refers to the time step.

[162]:
```
def Particules_initialise (Particule_Nbr, steps):

    Data_traj_list = np.zeros((4,steps))

    #Initial velocities : Thermal velocity with random direction
    vel = np.sqrt(k_b_mol * Temp / mass *10e-3)
    angle = np.random.uniform(0,2*np.pi)
    vx = np.sin(angle)*vel
    vy = np.cos(angle)*vel

    #Ramdom initial position
    x = np.random.uniform(2,3)
    y = np.random.uniform(2,3)

    Data_traj_list[:,0] = [x, y, vx, vy] #[data type, time step]

    return  Data_traj_list
```

Run Simulation

At the start of the simulation we already have the initial positions and velocities calculated. At each step we calculate :
* Position at time t+1 * Velocities at time t+1 : with the LE integrator * Storing both the velocities and position into our array

[163]:
```
def RUN ():
    check = []
    check2 = []

    for i in trange (0,steps-1,desc= 'Run the simulation'):
```

```
        Data_t = Data_traj_list[:,i]

        #calculat ing the position and implementing the periodic boundary␣
↪conditions
        x_1 = position (Data_t[0], Data_t[2], Dlt_t)%box[0]
        y_1 = position (Data_t[1], Data_t[3], Dlt_t)%box[1]

        v1_vec = LE_integrator([Data_t[2], Data_t[3]])

        # adding the particule position and velocity into the array
        Data_traj_list[0,i+1] = x_1
        Data_traj_list[1,i+1] = y_1
        Data_traj_list[2,i+1] = v1_vec[0]
        Data_traj_list[3,i+1] = v1_vec[1]

        check += [ v1_vec[0] ]
        check2 += [v1_vec[1]]
    return Data_traj_list, check, check2
```

Running the LE silulation Returning the "Data_traj_list" recoring the position and velocity at each time. And the "check" and "check2" which are the veck for the velocity along x and along y.

[164]:
```
Data_traj_list = Particules_initialise (Particule_Nbr, steps)
Data_traj_list, check, check2 = RUN()
```

```
HBox(children=(FloatProgress(value=0.0, description='Run the simulation', max=999999.0, style=I
```

[165]:
```
np.savez('save.npz', Data_traj_list)
```

Uploading data obtained with the MD simulation (ExVIII)

[166]:
```
npzfile = np.load('DataTraj_lastsave-EX8.npz')
Data_traj_total = npzfile['arr_0']

Data_traj_list0= Data_traj_total[16]
steps0 = 10000
time_list_plot0 = np.linspace(0,steps0,steps0)
```

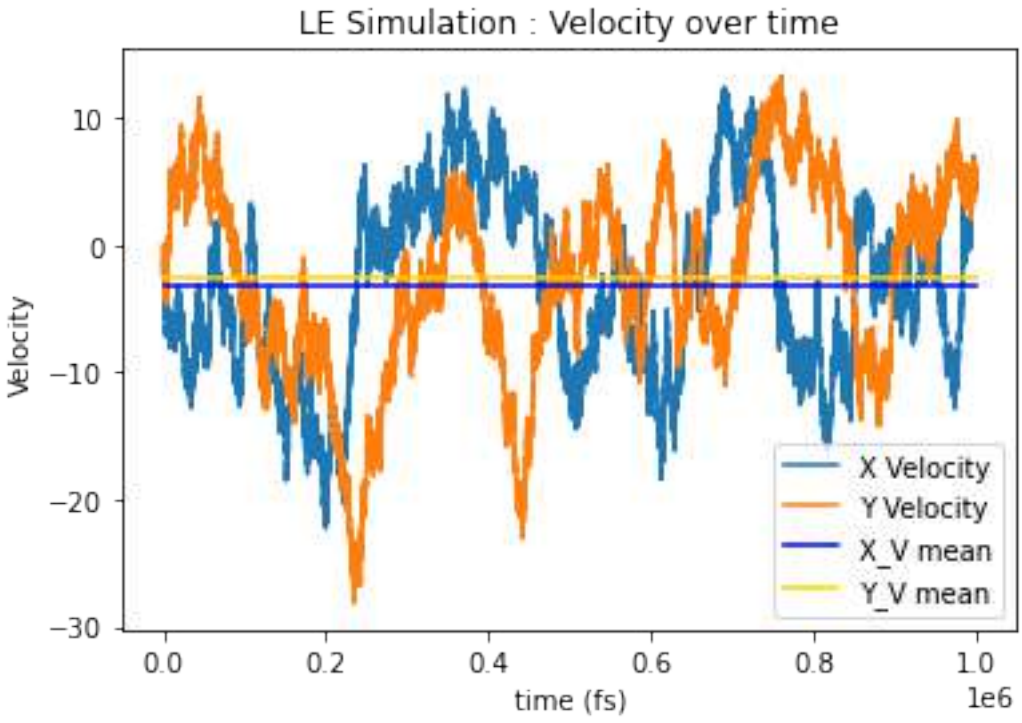
Checking that the velocities look correct

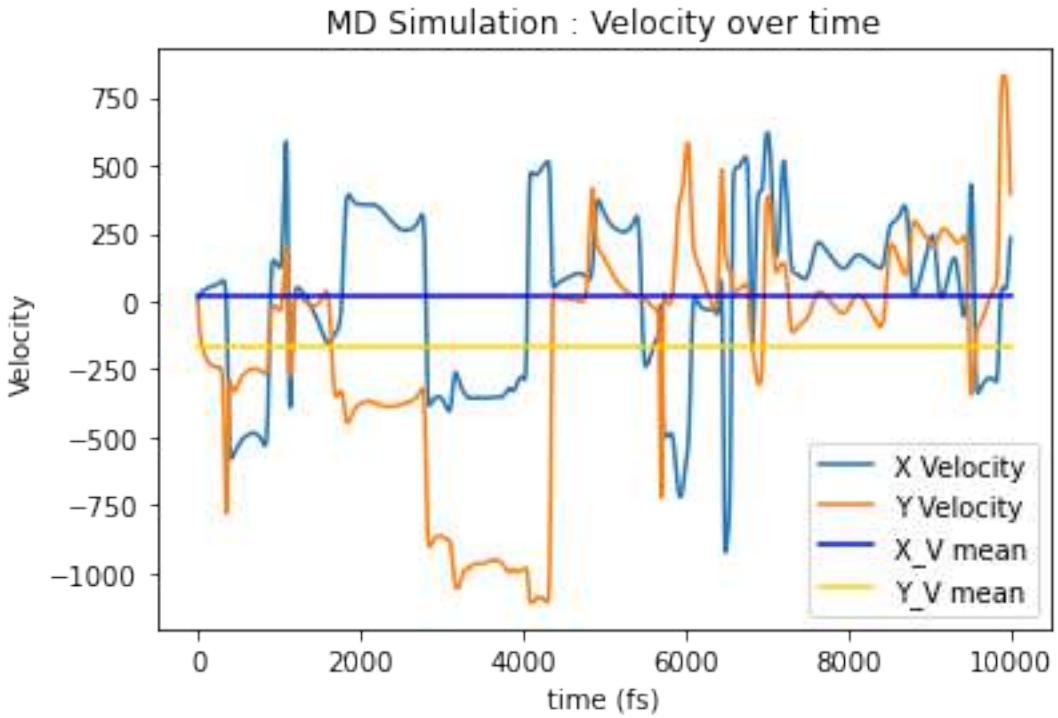
[167]:
```
def plot_vel(time_list_plot,check, check2, name ):
    plt.plot(time_list_plot, check, label = 'X Velocity')
    plt.plot(time_list_plot, check2, alpha = 1, label = 'Y Velocity')
```

```
    plt.plot([time_list_plot[0],time_list_plot[-1]], [np.mean(check), np.
↪mean(check)], color ='blue', label='X_V mean')
    plt.plot([time_list_plot[0],time_list_plot[-1]], [np.mean(check2), np.
↪mean(check2)], color ='Gold', label='Y_V mean')
    #total_mean = np.sqrt(np.mean(check)**2+np.mean(check2)**2)
    #plt.plot([time_list_plot[0],time_list_plot[-1]], [total_mean, total_mean],␣
↪linestyle='--', color ='Black')

    plt.xlabel('time (fs)')
    plt.ylabel('Velocity')

    t = name + ' Simulation : Velocity over time'
    plt.title(t)
    plt.legend()
    plt.show()
```

[168]:
```
plot_vel(time_list_plot,check, check2, 'LE' )

v_x = Data_traj_list0[2,:]
v_y = Data_traj_list0[3,:]
plot_vel(time_list_plot0, v_x, v_y, 'MD' )
```

```
/home/lea/anaconda3/lib/python3.8/site-packages/IPython/core/pylabtools.py:132:
UserWarning: Creating legend with loc="best" can be slow with large amounts of
data.
  fig.canvas.print_figure(bytes_io, **kw)
```



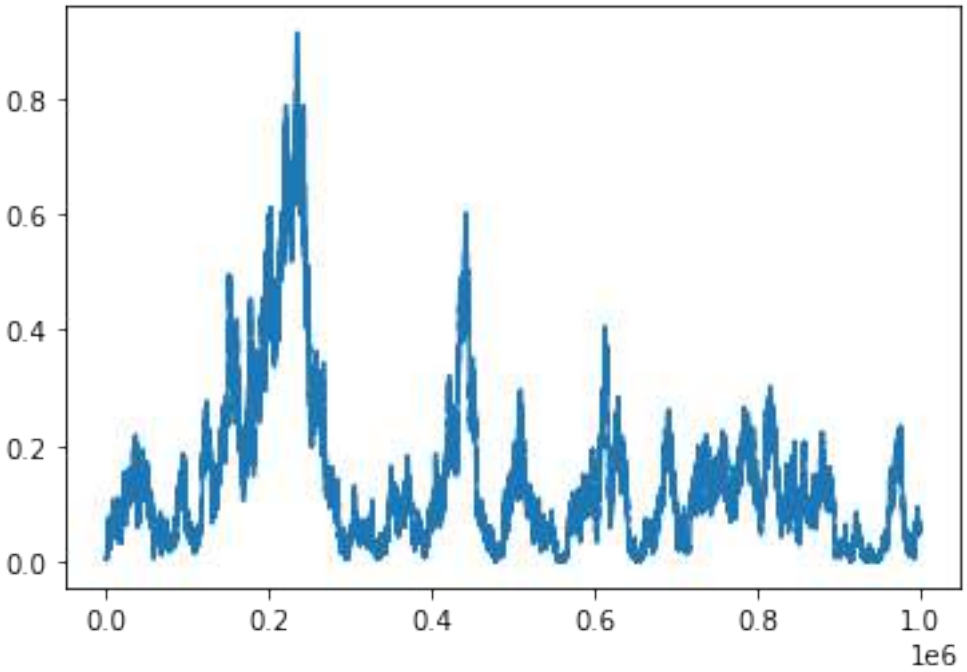


[169]:
```
K= []
T = []
for i in trange(steps):
    K += [Kinetic(Data_traj_list, i)]
    T += [Kinetic(Data_traj_list, i)/k_b_mol]
```

```
HBox(children=(FloatProgress(value=0.0, max=1000000.0), HTML(value='')))
```

[170]:
```
plt.plot(time_list_plot, T[:-1])
```

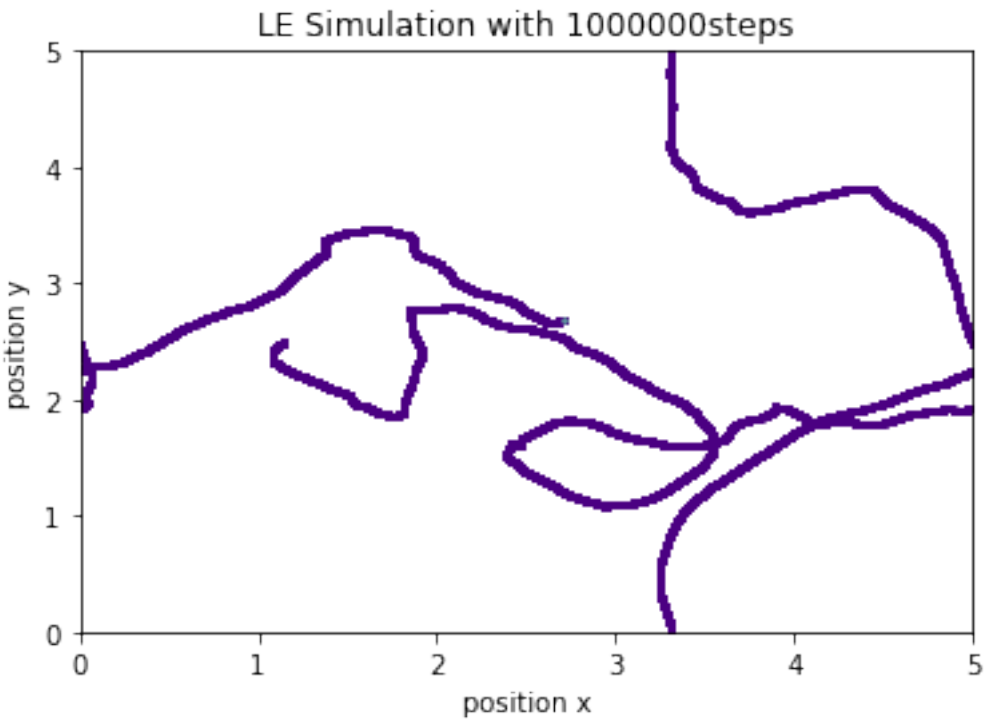
[170]: [<matplotlib.lines.Line2D at 0x7fa0aa7d6cd0>]



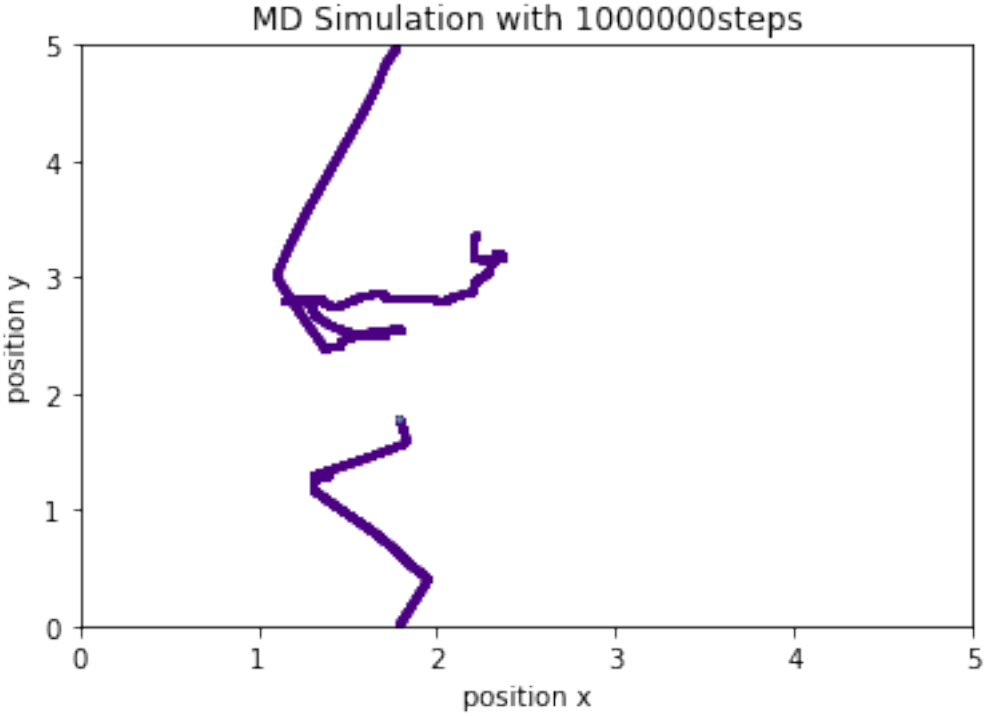
My integrator is probably wrong as my speed s too low, both compared to the MD simulation and to the Temperature calculated from the kinetic enery.

Checking that the trajectories look correct

[171]:
```
x, y =plot(Data_traj_list, 'LE')
```



[172]:
```
x, y =plot(Data_traj_list0, 'MD')
```



2.3.1 Video

[173]:
```
def creat_files(data_traj, steps):
    os.chdir("Image_storing_video")
    c = 'indigo'

    for t in trange (steps) :
        if t%5==0:
            plt.plot(data_traj[0,0],data_traj[1,0], marker='.',␣
↪markersize='10',  linestyle = '-', alpha=0.3, color = c)
            plt.plot(data_traj[0,t],data_traj[1,t], marker='.',␣
↪markersize='10',  linestyle = '-', color = c)

            #plt.show()
            plt.xlabel('position x')
            plt.ylabel('position y')
            plt.xlim(0,box[0])
            plt.ylim(0,box[1])
            plt.savefig("File%02d.png" % t)
    #plt.show()
    #plt.savefig("file.png")
    plt.close()



    Titles_graph1 = 'Example of one of the simulation of with' + str(steps) +␣
↪'steps'
    plt.title(Titles_graph1)
    os.chdir("../")
```

[174]:
```
def creat_video():
    os.chdir("Image_storing_video")

    subprocess.call(['ffmpeg', '-framerate', '5', '-i', 'File%02d.png', '-r',␣
↪'30', '-pix_fmt', 'yuv420p', 'Contagion08.mp4'])
    #subprocess.call(['ffmpeg', '-framerate', '8', '-i', Titles_files, '-r',␣
↪'30', '-pix_fmt', 'yuv420p', Filename])


    for file_name in glob.glob("*.png"):
        os.remove(file_name)

    os.chdir("../")
```

[175]:
```
'''
retval = os.getcwd()
print ("Current working directory %s" % retval)
creat_files(Data_traj_list0, steps0)
creat_video()
'''
```

[175]:
```
'\nretval = os.getcwd()\nprint ("Current working directory %s" %
retval)\ncreat_files(Data_traj_list0, steps0)\ncreat_video()\n'
```

[176]:
```
#os.chdir("../")
```

2.4 Task III: Determination of diffusion coefficient

Diffusion coefficient :

$$D = \frac{\Delta\vec{x}(t)^2}{4t}$$

with $\Delta\vec{x}(t)^2 = (\vec{x}(t) - \vec{x}(t_0))^2 = \Delta x_x(t)^2 + \Delta x_y(t)^2$

[177]:
```
def Diff_coef(t, Data_traj_list):
    #This function get_vect_r returns the conecting vection between two␣
 ↪positions
    # taking into account the periodic bounday conditions
    [Dlt_x, Dlt_y] = get_vect_r(Data_traj_list[0,0],Data_traj_list[1,0],␣
 ↪Data_traj_list[0,t], Data_traj_list[1,t])

    D = (Dlt_x**2 + Dlt_y**2)/(4*t)
    Dltx = (Dlt_x**2 + Dlt_y**2)
    return D, Dltx
```

Fricction coefficient

$$\Gamma = \frac{k_b T}{D}$$

[178]:
```
def Fric_coef(D):
    Gamma = k_b * Temp / D
    return Gamma
```

Calculation of D and Δx^2

[179]:
```
D_list = []
Dltx_list = []
Gamma_list = []

for t in trange(1,steps-1):
    D, Dltx = Diff_coef(t, Data_traj_list)
    D_list += [D]
    Dltx_list += [Dltx]
```

```
    Gamma_list += [Fric_coef(D)]
```

```
HBox(children=(FloatProgress(value=0.0, max=999998.0), HTML(value='')))
```

[180]:
```
D_list0 = []
Dltx_list0 = []
Gamma_list0 = []

for t in trange(1,steps0-1):
    D0, Dltx0 = Diff_coef(t, Data_traj_list0)
    D_list0 += [D0]
    Dltx_list0 += [Dltx0]
    Gamma_list0 += [Fric_coef(D0)]
```

```
HBox(children=(FloatProgress(value=0.0, max=9998.0), HTML(value='')))
```

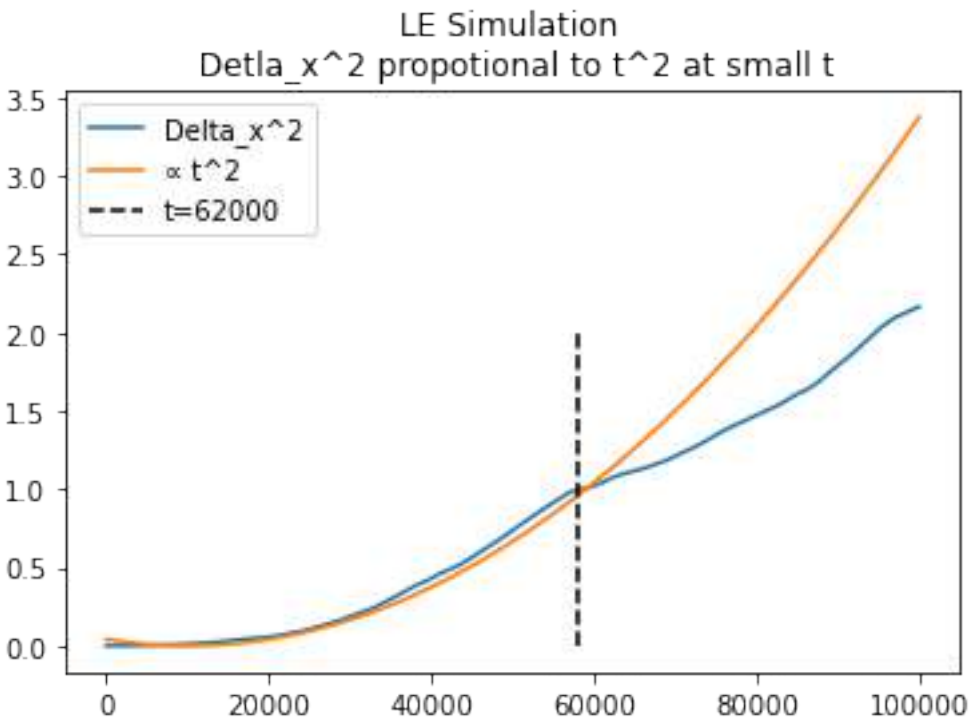
Analysis of the evolution of Δx^2

We can clearly see that for small values of t (< 58000), Δx^2 is propotional to t^2. And after that the particle follows a diffusive behavior, therefore it should evolve linearly with t for large time scales.

- Quadratic fit : $(t - 10000)^2 4.16 * 10^{-10}$

[241]:
```
t_sqrd = []
for t in time_list_plot:
    t_sqrd += [(t-10000)**2 * 1.5/60000**2 ]
```

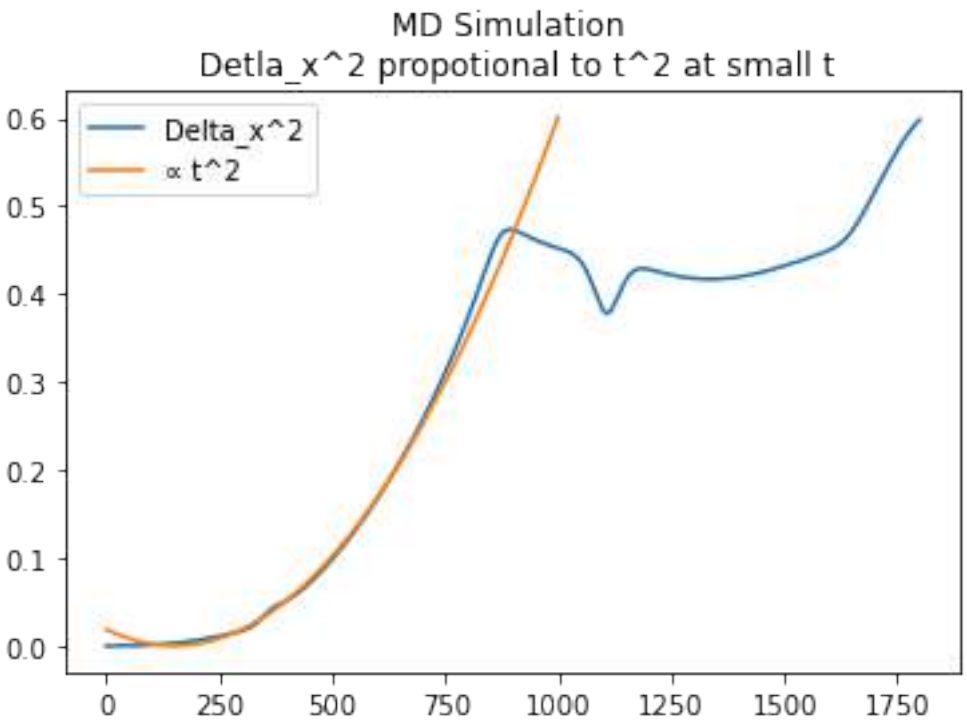
[244]:
```
plt.plot(time_list_plot[:100000], Dltx_list[:100000], label ='Delta_x^2')
plt.plot(time_list_plot[:100000], t_sqrd[:100000], label = '  t^2')
plt.plot([58000,58000], [0,2],linestyle='--', color='Black', label='t=62000')
#plt.plot([22000,22000], [t_sqrd[0],t_sqrd[-1]],linestyle='--', color='Black',␣
↪alpha = 0.3, label='t=22000')
plt.legend()
a=plt.title('LE Simulation \n Detla_x^2 propotional to t^2 at small t')
```



- Quadratic fit : $(t-150)^2/12 * 10^{-5}$

[337]:
```
t_sqrd0 = []
for t in time_list_plot0:
    t_sqrd0 += [(t-150)**2 * 1/1200000 ]
```

[338]:
```
plt.plot(time_list_plot0[:1800], Dltx_list0[0:1800], label ='Delta_x^2')
plt.plot(time_list_plot0[:1000], t_sqrd0[:1000], label = '  t^2')
#plt.plot([62000,62000], [t_sqrd[0],t_sqrd[-1]],linestyle='--', color='Black',␣
 ↪label='t=62000')
#plt.plot([22000,22000], [t_sqrd[0],t_sqrd[-1]],linestyle='--', color='Black',␣
 ↪alpha = 0.3, label='t=22000')
plt.legend()
a=plt.title('MD Simulation \n Detla_x^2 propotional to t^2 at small t')
```



Analysis of D

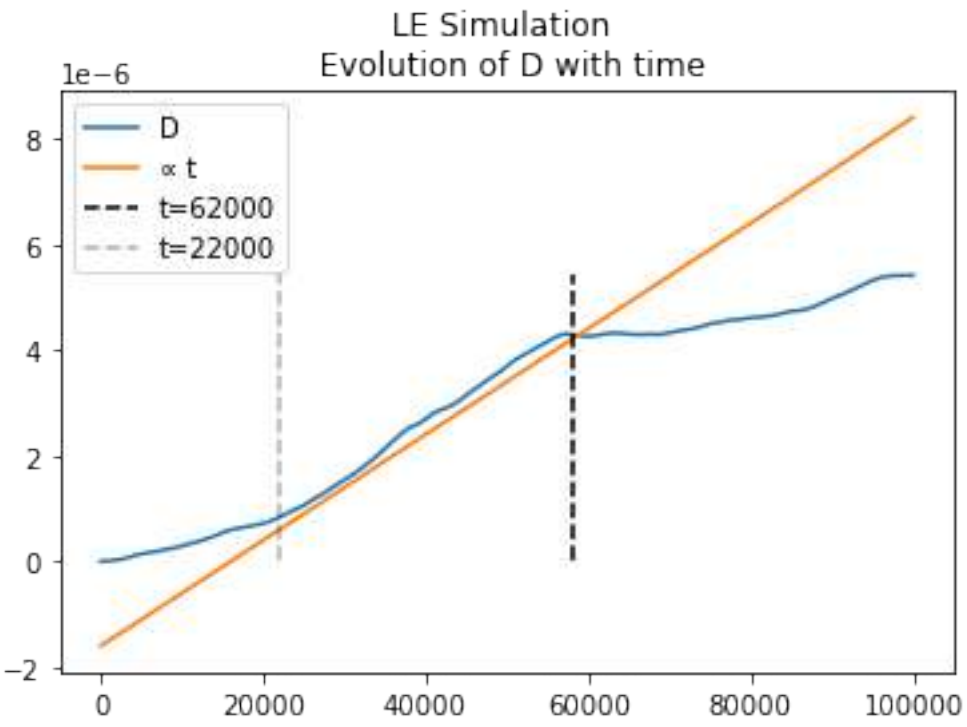
We can see that beween 22000 and 62000 the evolution of D follows a linear evolution in function of t, which is consistant with an evolution proportionalto t^2 for Δx^2.

- Linear fit of t : $(t - 16000)10^{-11}$

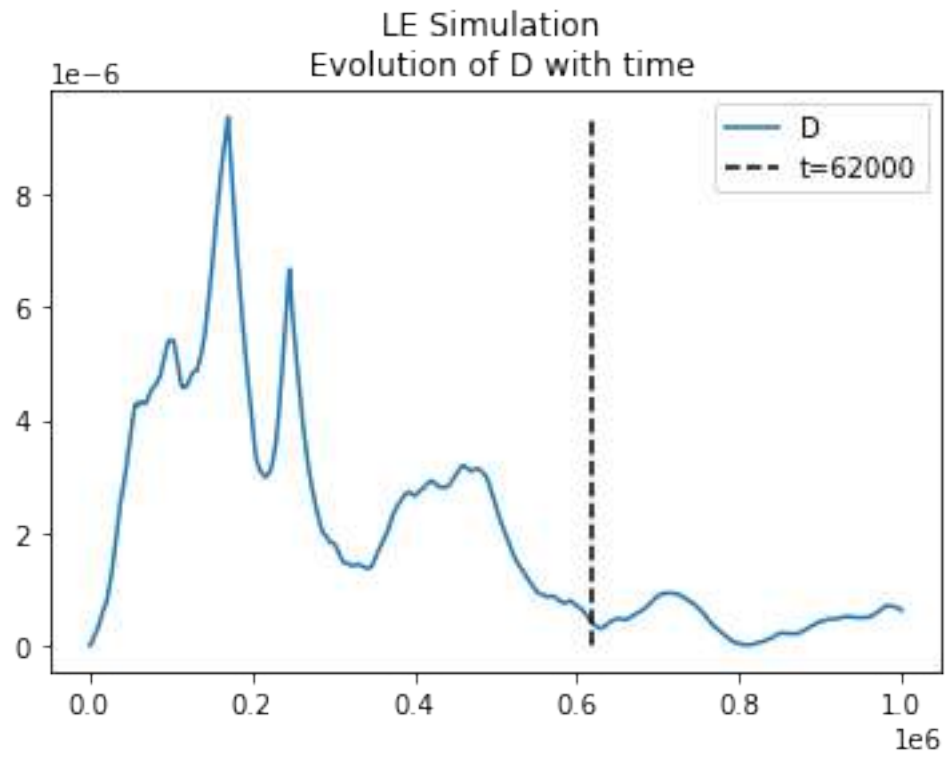
For low values of t ($22000 < t < 58000$) D follows an evolution linear in t. Which correspond to our the fact that Δx^2 is propotional to t^2 at low t.

[215]:
```
t_lin = []
for t in time_list_plot:
    t_lin += [(t-16000) * 10e-11]
```

[220]:
```
plt.plot(time_list_plot[:100000], D_list[:100000], label ='D')
plt.plot(time_list_plot[:100000], t_lin[:100000], label = ' t')
plt.plot([58000,58000], [min(D_list[:100000]),max(D_list[:
 ↪100000])],linestyle='--', color='Black', label='t=62000')
plt.plot([22000,22000], [min(D_list[:100000]),max(D_list[:
 ↪100000])],linestyle='--', color='Black', alpha=0.3, label='t=22000')
plt.legend()
a=plt.title('LE Simulation \n Evolution of D for small time')
```



[223]:
```
plt.plot(time_list_plot[1:], D_list, label ='D')
#plt.plot(time_list_plot[22000:62000], t_lin[22000:62000], label = ' t')
plt.plot([620000,620000], [min(D_list),max(D_list)],linestyle='--',␣
↪color='Black', label='t=62000')
#plt.plot([22000,22000], [min(D_list),max(D_list)],linestyle='--',␣
↪color='Black', alpha=0.3, label='t=22000')
plt.legend()
a=plt.title('LE Simulation \n Evolution of D with time')
```



Interpretation of the results

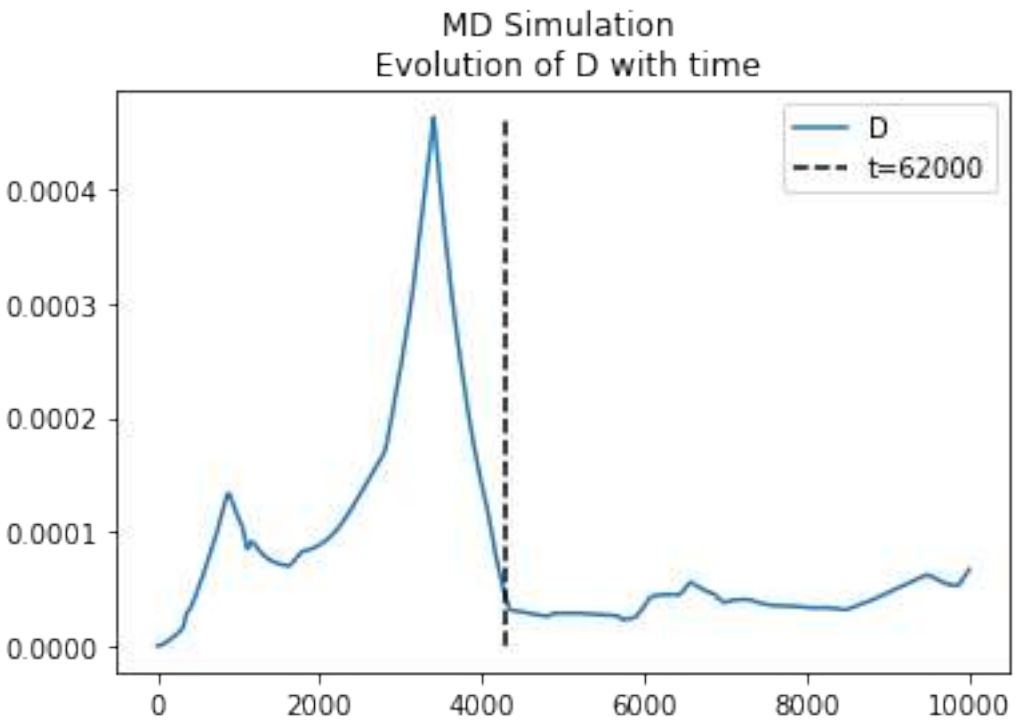
[258]:
```
D_mean = np.mean(D_list[620000])*10e-3
print(D_mean, 'in m^2/s')
```

```
3.816757674740708e-09 in m^2/s
```

As expected Δx^2 is proportional to t^2 for small t and accordingly D is propotional to t. This time the initial velocity takes until it follows diffusive behavior seem to last until 58000fs.

D = 3.82 10^-9 m^2/s seems to be a reasonable result as for the diffusion for molecules dissolved in an aqueous solution, typical diffusion coefficients are in the range of 10^{-10} to $10^{-9} m^2/s$.

[248]:
```
plt.plot(time_list_plot0[1:-1], D_list0, label ='D')
#plt.plot(time_list_plot[22000:62000], t_lin[22000:62000], label = ' t')
plt.plot([4300,4300], [min(D_list0),max(D_list0)],linestyle='--',␣
 ↪color='Black', label='t=62000')
#plt.plot([22000,22000], [min(D_list),max(D_list)],linestyle='--',␣
 ↪color='Black', alpha=0.3, label='t=62000')
plt.legend()
a=plt.title('MD Simulation \n Evolution of D with time')
```



[254]:
```
D_mean0 = np.mean(D_list0[4300:])*10e-3
print(D_mean0, 'in m^2/s')
```

```
3.9119398931004695e-07 in m^2/s
```

$D_0 = 3.91e-7 m^2/s$ seems also to be an acceptable result but would correspond more to a diffusion coefficient for a molecule in the gas phase. Which has a range 10^{-6} and 10^{-5} although it seems a bit too low for that.

Second observation is that the velocity of the particle for in LE simulation is much lower the for the MD simulation. This might be a misktake in the LE intergrator, yeilding very low velocities or a wrong value of gamma given initially. But we can still observe that in LE simulation we have low velocities, yeilding a lower D then for the MD one. Which in turns correspond to molocules in a liquid phase for LEs, with therefore lower velocities then in a gas phase described my the MD simulation (according to the value found of D_0.

We can see that in the MD simulation we reach the diffusive behavious quicker, which maybe due, once again, to higher velocities the in the LE simulation.

Analysis of Γ

Γ is propotional to the inverse of D.

[268]:
```
print('LE simulation : \n', 'D = ', D_mean, 'm^2/s \n', 'Gamma = ',␣
↪Fric_coef(D_mean), 'Kg/s')
print()
```

```
print('MD simulation : \n', 'D0 = ', D_mean0, 'm^2/s \n', 'Gamma_0 = ',␣
 ↪Fric_coef(D_mean0), 'Kg/s')
```

```
LE simulation :
 D =  3.816757674740708e-09 m^2/s
 Gamma =  1.0604216689693192e-12 Kg/s

MD simulation :
 D0 =  3.9119398931004695e-07 m^2/s
 Gamma_0 =  1.034620330092084e-14 Kg/s
```

Conclusion

Overall the simmulation seems to run correctly as we can see that the average velocities are close to zero for both LE and MD simulations. The off set might be due to the initial velocity, as for example we wan see in the plot of the LE simulation, we are starting with an initial velocity with both x and y componant negative, and the off set is also negativ for both x and y componant of the velocity.

The trajectorry of the particles for both LE and MD simulation seems to match what we expect. One of the major different is that is the LE simulation runs for 10000 steps the particle barely mooves. This was confirmed by the calculation of the Kineic energy and then the plot of the temperature over time. Which looks very wrong and with too low values. Maybe it is a wrong implementation of the LE intergrator, or a value for gamma is too low or high. I have tried to change it but it resulted in my simulation either wa too slow or mysystem exploding.

Using the results obtained from the simulation decribed above we obtained resonable results. First we checked that Δx^2 was proportional to t^2 for small t and accordingly D was propotional to t, which holds well for both LE and MD simulation.

Then averaging D for large t, we obtained our value of Diffusion coefficient. Which when compared to typical diffusions coefficents they seem to be resonable values to obtain, and the difference in order of magnitude is coherent with the different of velocity in the two simulations.

LE : D = 3.817e-9
MD : D0 = 3.912e-7

We then calculated to fricction coefficient for both simulations. Surprisingly the value for LE simulation does not match the one of the Gamma given initially, once again that might come from a problem in the LE intergrator resulting in a lower Gamma overall. :

LE : Gamma = 1.060e-12 Kg/s
LE (initial value given) Gamma = 2.1e-13 Kg/s
MD : Gamma_0 = 1.035e-14 Kg/s

[ ]: