1a (i) $|\vec{p}_i|^2 = |\vec{p}_i| \cdot |\vec{p}_i| = \begin{pmatrix} p_i^x & p_i^y & p_i^z \end{pmatrix} \cdot \begin{pmatrix} p_i^x \\ p_i^y \\ p_i^z \end{pmatrix} = \left((p_i^x)^2 + (p_i^y)^2 + (p_i^z)^2\right)$

$$\frac{\partial |\vec{p}_i|^2}{\partial \vec{p}_i} = \frac{\partial}{\partial \vec{p}_i}\left((p_i^x)^2 + (p_i^y)^2 + (p_i^z)^2\right) = \left(\frac{\partial}{\partial p_i^x}\left((p_i^x)^2 + (p_i^y)^2 + (p_i^z)^2\right)\right.$$

$$\left. \frac{\partial}{\partial p_i^y}\left((p_i^x)^2 + (p_i^y)^2 + (p_i^z)^2\right) \quad \frac{\partial}{\partial p_i^z}\left((p_i^x)^2 + (p_i^y)^2 + (p_i^z)^2\right)\right)$$

$$= \left(\frac{\partial (p_i^x)^2}{\partial p_i^x} \quad \frac{\partial (p_i^y)^2}{\partial p_i^y} \quad \frac{\partial (p_i^z)^2}{\partial p_i^z}\right) = \begin{pmatrix} 2p_i^x & 2p_i^y & 2p_i^z \end{pmatrix}$$

$$= 2\begin{pmatrix} p_i^x & p_i^y & p_i^z \end{pmatrix} = 2\vec{p}_i$$

$$\rightarrow \frac{1}{2m_i}\frac{\partial |\vec{p}_i|^2}{\partial \vec{p}_i} = \frac{2\vec{p}_i}{2m_i} = \boxed{\frac{\vec{p}_i}{m_i}}$$

(ii) $$r_{ij} = \sqrt{(r_i^x - r_j^x)^2 + (r_i^y - r_j^y)^2 + (r_i^z - r_j^z)^2}$$

$$\frac{\partial r_{ij}}{\partial \vec{r}_i} = \begin{pmatrix} \frac{\partial r_{ij}}{\partial r_i^x} & \frac{\partial r_{ij}}{\partial r_i^y} & \frac{\partial r_{ij}}{\partial r_i^z} \end{pmatrix}$$

$$\cdots \frac{\partial r_{ij}}{\partial r_i^x} = \frac{1}{2}\left((r_i^x - r_j^x)^2 + (r_i^y - r_j^y)^2 + (r_i^z - r_j^z)^2\right)^{-\frac{1}{2}} \cdot 2(r_i^x - r_j^x)$$

$$= \frac{(r_i^x - r_j^x)}{r_{ij}} \rightarrow \frac{\partial r_{ij}}{\partial r_i^y} = \frac{(r_i^y - r_j^y)}{r_{ij}} \; ; \; \frac{\partial r_{ij}}{\partial r_i^z} = \frac{(r_i^z - r_j^z)}{r_{ij}}$$

$$= \begin{pmatrix} \frac{r_i^x - r_j^x}{r_{ij}} & \frac{r_i^y - r_j^y}{r_{ij}} & \frac{r_i^z - r_j^z}{r_{ij}} \end{pmatrix} = \frac{1}{r_{ij}}\begin{pmatrix} (r_i^x - r_j^x) & (r_i^y - r_j^y) & (r_i^z - r_j^z) \end{pmatrix}$$

$$= \frac{1}{r_{ij}}\begin{pmatrix} r_{ij}^x & r_{ij}^y & r_{ij}^z \end{pmatrix} = \boxed{\frac{\vec{r}_{ij}}{r_{ij}}}$$

(iii) TOTAL MOMENTUM $= \sum \vec{p}_i \equiv \vec{P}$

IF HAMILTON'S EQ. CONSERVE $\vec{P}_j$, THEN $\{\vec{P}_j, \mathcal{H}\} = 0$.

LETS CHECK!

$$\{\cdot, \mathcal{H}\} = \sum_j \left[\frac{\partial \cdot}{\partial \vec{r}_j} \frac{\partial \mathcal{H}}{\partial \vec{p}_j} - \frac{\partial \cdot}{\partial \vec{p}_j} \frac{\partial \mathcal{H}}{\partial \vec{r}_j} \right]$$

$$\{\vec{P}, \mathcal{H}\} = \sum_j \left[\frac{\partial \vec{P}}{\partial \vec{r}_j} \frac{\partial \mathcal{H}}{\partial \vec{p}_j} - \frac{\partial \vec{P}}{\partial \vec{p}_j} \frac{\partial \mathcal{H}}{\partial \vec{r}_j} \right]$$

$$= \sum_j \left[\frac{\partial}{\partial \vec{r}_j} \left[\sum_i \vec{p}_i \right] \frac{\partial \mathcal{H}}{\partial \vec{p}_j} - \frac{\partial}{\partial \vec{p}_j} \left[\sum_i \vec{p}_i \right] \frac{\partial \mathcal{H}}{\partial \vec{r}_j} \right]$$

$\vec{p}_i$ DOESN'T DEPEND ON $\vec{r}_j$ SO ALL TERMS IN $\left(\frac{\partial \vec{p}_1}{\partial \vec{r}_j} + \frac{\partial \vec{p}_2}{\partial \vec{r}_j} + \ldots \right) = 0$.

WHEN $\vec{p}_i \neq \vec{p}_j$, $\frac{\partial \vec{p}_i}{\partial \vec{p}_j} = 0$

SO WE ARE LEFT WITH ONLY $\vec{p}_i = \vec{p}_j$ IN THE SUM OVER i.

$$\{\vec{P}, \mathcal{H}\} = -\sum_j \left[\frac{\partial \vec{p}_j}{\partial \vec{p}_j} \frac{\partial \mathcal{H}}{\partial \vec{r}_j} \right] = -\sum_j \frac{\partial \mathcal{H}}{\partial \vec{r}_j} = -\sum_j \frac{\partial U}{\partial \vec{r}_j} = \sum_j \vec{F}_j$$

$\therefore \{\vec{P}, \mathcal{H}\} = \sum_j \vec{F}_j$ $\therefore$ THE TOTAL FORCE ACTING ON THE SYSTEM; WHEN THERE IS NO EXTERNAL FORCE ACTING ON THE SYSTEM (i.e. $\mathcal{H}$ IS CONSERVED), THEN THE TOTAL MOMENTUM IS ALSO CONSERVED.

1b

VERLET $\begin{cases} r_i(t+\Delta t) = 2r_i(t) - r_i(t-\Delta t) + \frac{(\Delta t)^2}{2}\frac{F_i(t)}{m_i} \\ V_i(t) = \frac{r_i(t+\Delta t) - r_i(t-\Delta t)}{2\Delta t} \end{cases}$

$\rightarrow r_i(t-\Delta t) = r_i(t) - \Delta t\, V_i(t) + \frac{(\Delta t)^2}{2}\frac{F_i(t)}{m}$

$\therefore$ TAKE $t-\Delta t$ TO BE $t+\Delta t$; EVOLVE BACKWARD IN TIME t

$r_i(t) = r_i((t+\Delta t)-\Delta t) = r_i(t+\Delta t) - \Delta t\, V_i(t+\Delta t) + \frac{(\Delta t)^2}{2}\frac{F_i(t+\Delta t)}{m_i}$

~~PLUG IN THE VERLET EXPRESSION FOR $r_i(t+\Delta t)$~~

$r_i(t) = \left[r_i(t) - r_i(t-\Delta t) + \frac{(\Delta t)^2 F_i(t)}{2 m_i}\right] - \Delta t\, V_i(t+\Delta t) + \frac{(\Delta t)^2}{2}\frac{F_i(t+\Delta t)}{m_i}$

PLUG IN TAYLOR EXPANSION FOR $r_i(t+\Delta t)$

$r_i(t) = \left[r_i(t) + \Delta t\, V_i(t) + \frac{(\Delta t)^2}{2}\frac{F_i(t)}{m}\right] - \Delta t\, V_i(t+\Delta t) + \frac{(\Delta t)^2}{2}\frac{F_i(t+\Delta t)}{m_i}$

$V_i(t+\Delta t) = V_i(t) + \frac{\Delta t}{2m_i}\left[F_i(t) + F_i(t+\Delta t)\right]$

$V_i(t+\Delta t) = \frac{1}{2}\left[V_i(t+\frac{\Delta t}{2}) + V_i(t-\frac{\Delta t}{2})\right] + \frac{\Delta t}{2m_i}\left[F_i(t) + F_i(t+\Delta t)\right]$

LEAP FROG ↑ PLUG IN LEAP FROG

$V_i(t+\Delta t) = \frac{1}{2}V_i(t+\frac{\Delta t}{2}) + \frac{1}{2}\left[V_i(t+\frac{\Delta t}{2}) - \Delta t\frac{F_i(t)}{m_i}\right] + \frac{\Delta t}{2m_i}\left[F_i(t) + F_i(t+\Delta t)\right]$

$V_i(t+\Delta t) = V_i(t+\frac{\Delta t}{2}) + \frac{\Delta t}{2m_i}F_i(t+\Delta t)$ $\therefore$ V.V. 3

$V_i(t+\frac{\Delta t}{2}) = V_i(t+\Delta t) - \frac{\Delta t}{2m_i}F_i(t+\Delta t)$

$V_i(t+\frac{\Delta t}{2}) = V_i(t) + \frac{\Delta t}{2m_i}\left[F_i(t) + F_i(t+\Delta t)\right] - \frac{\Delta t}{2m_i}F_i(t+\Delta t)$

$V_i(t+\frac{\Delta t}{2}) = V_i(t) + \frac{\Delta t}{2m_i}F_i(t)$ $\therefore$ V.V. 1

$$r_i(t+\Delta t) = r_i(t) + \Delta t\, V_i(t) + \frac{(\Delta t)^2}{2m} F_i(t)$$

V.V. 1 = $V_i\left(t+\frac{\Delta t}{2}\right) = V_i(t) + \frac{\Delta t}{2m_i} F_i(t)$

$$F_i(t) = \frac{2m}{\Delta t}\left[V_i\left(t+\tfrac{\Delta t}{2}\right) - V_i(t)\right]$$

$$r_i(t+\Delta t) = r_i(t) + \Delta t\, V_i(t) + \frac{(\Delta t)^2}{\Delta t}\frac{2m}{2m}\left[V_i(t+\Delta t) - V_i(t)\right]$$

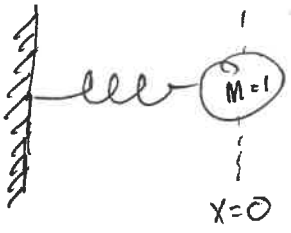
$$= r_i(t) + \Delta t\, V_i(t) - \Delta t\, V_i(t) + \Delta t\, V_i(t+\Delta t)$$

$$\boxed{r_i(t+\Delta t) = r_i(t) + \Delta t\; V_i(t+\Delta t)}$$ ∴ V.V. 2

∴ THIS IS THE SAME THING AS IN LEAP FROG! :)

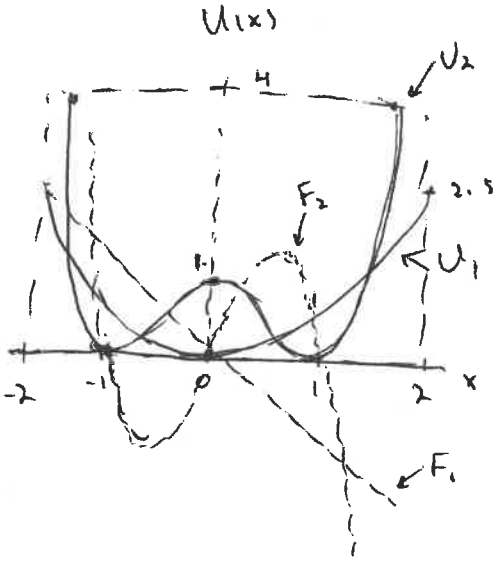
2

$m=1$, $U_1 = \frac{x^2}{2}$, $U_2 = x^4 - 2x^2 + 1$



$$F = -\frac{\partial U}{\partial x} \rightarrow F_1 = -\frac{\partial}{\partial x}\left[\frac{x^2}{2}\right] = -x$$

$F_1 = -x$ $[k \equiv 1]$



$F_2 = -4x^3 + 4x$

NEXT PAGE...

2a

$$\dot{x}_1 \equiv \frac{\partial H}{\partial p_1} = \frac{d}{dp}\left(\frac{p_1^2}{2m}\right) = \frac{p_1}{m} = v_1 = \dot{x}_1$$

$$\dot{p}_1 = -\frac{\partial H}{\partial x} = -\frac{\partial U}{\partial x} = -\frac{\partial}{\partial x}\left(\frac{x^2}{2}\right) = -x = F_1 = \dot{p}_1$$

$$\dot{x}_2 = \frac{\partial H}{\partial p_2} \quad \frac{\partial}{\partial p}\left(\frac{p_2^2}{2m}\right) = \frac{p_2}{m} = v_2 = \dot{x}_2$$

$$\dot{p}_2 = -\frac{\partial H}{\partial x} = -\frac{\partial U}{\partial x} = -\frac{\partial}{\partial x}\left(x^4 - 2x^2 + 1\right) = -4x^3 + 4x = F_2 = \dot{p}_2$$

b) ~~$F_1 = F_2$~~ Newtons 2nd law → $F = ma$; $F = m\frac{d^2x}{dt^2}$

For 1, we saw $F_1 = -x$

→

1. $m\frac{d^2x}{dt} = -x$ → ~~$x =$~~

2. $m\frac{\partial^2 x}{\partial x} = -4x^3 + 4x$

∴ solutions are sine & cos → superpos. is also a sol.

$$x(t) = x_0 \cos\left(\frac{1}{\sqrt{m}}t\right) + v_0 \sin\left(\frac{1}{\sqrt{m}}t\right)$$

$$v(t) = -\frac{x_0}{\sqrt{m}}\sin\left(\frac{1}{\sqrt{m}}t\right) + \frac{v_0}{\sqrt{m}}\cos\left(\frac{1}{\sqrt{m}}t\right)$$

case 2: not solvable ☺

For v: $m\frac{dv}{dt} = -x$

PLOT ON NEXT PAGE!

$$\text{Energy} = \frac{1}{2}m(v(t))^2 = \frac{1}{2}v^2 = \frac{p^2}{2} + \frac{x^2}{2} \; ; \; H = \frac{p^2}{2} + U(x)$$

$$\{E, H\} = \left[\frac{\partial E}{\partial x}\frac{\partial H}{\partial p} - \frac{\partial E}{\partial p}\frac{\partial H}{\partial x}\right] = \left[xp - px\right] = 0$$

∴ energy is conserved.

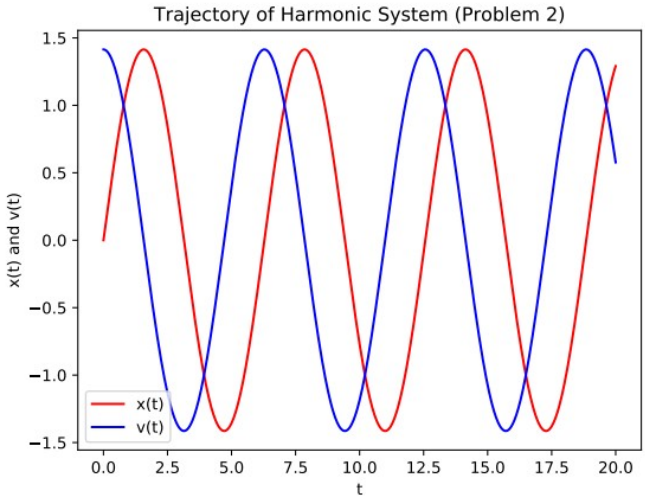
~~$\frac{\partial E}{\partial x} = \frac{\partial p^2}{\partial x} = 0$~~

$$\{p, H\} = \left[\frac{\partial p}{\partial x}\frac{\partial H}{\partial p} - \frac{\partial p}{\partial p}\frac{\partial H}{\partial x}\right] = -x$$ ∴ momentum not

conserved; i.e. there is a space-dependent force acting on the mass → the momentum is always changing, i.e. not conserved.

Note: When looking at my code, just consider the script ‘problem2fx.py’ in the zip folder. The other folders, ‘linear’ and ‘nonlinear’ contain the scripts where I call my MD functions from problem2fx.py, i.e. the scripts that make the plots. You can run them if you want; they should work, but are not easy to read through. ‘problem2fx.py’ IS easy to read through.

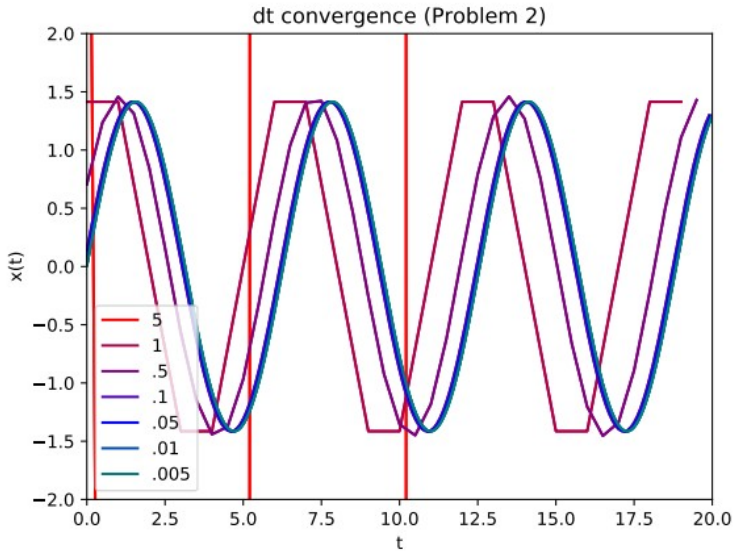
Here is my plot of the analytical trajectory:



The position and velocity are sine and cosines (or vise versa) as expected, i.e. the position is 90 degrees out of phase with the velocity. This is a well known results for a simple harmonic oscillator.

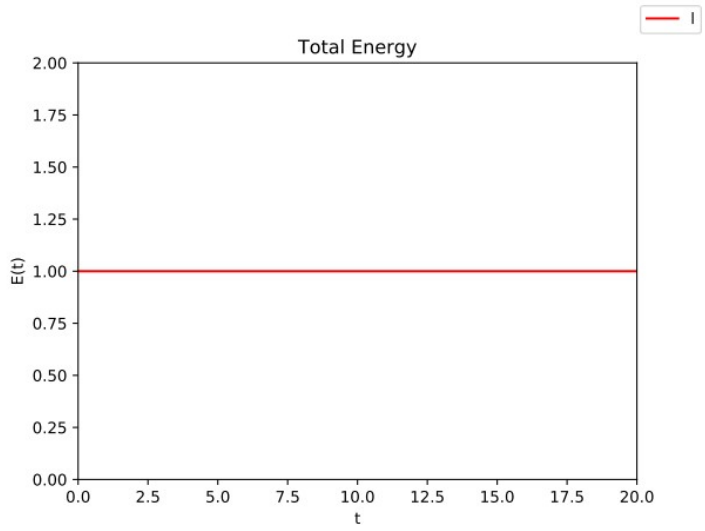
The proof of conservation of energy and non-conservation of momentum are on the previous page.

MD solution to linear spring: After writing my MD code, I ran a convergence study with a range of time steps. I picked the smallest timestep that converged on the expected trajectory, i.e. 0.01 (no units). I wanted a small enough step the Verlet algorithm is still valid, but long enough that my code wouldn’t take too long. Here is my convergence study:



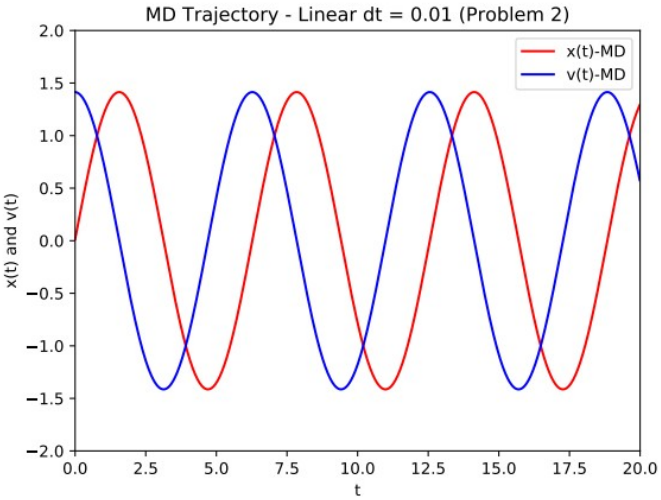
the trajectories diverge for dt = 5, is coarse for 1, and approaches the converged trajectory at 0.5. The simulation time wasn't too long, so I picked 0.01 as this gives good results with reasonable cost.

We can show that the energy is conserved by plotting the total energy as a function of time:



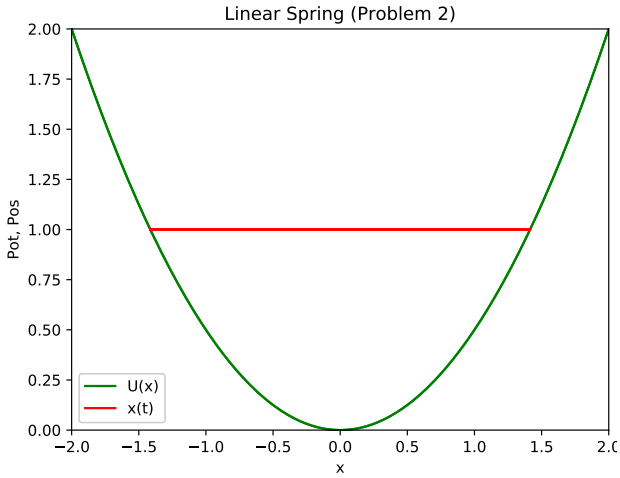
The total energy maintains it's initial value of E = 1 for the duration of the simulation; this is the same way that we check conservation of energy in LAMMPS.

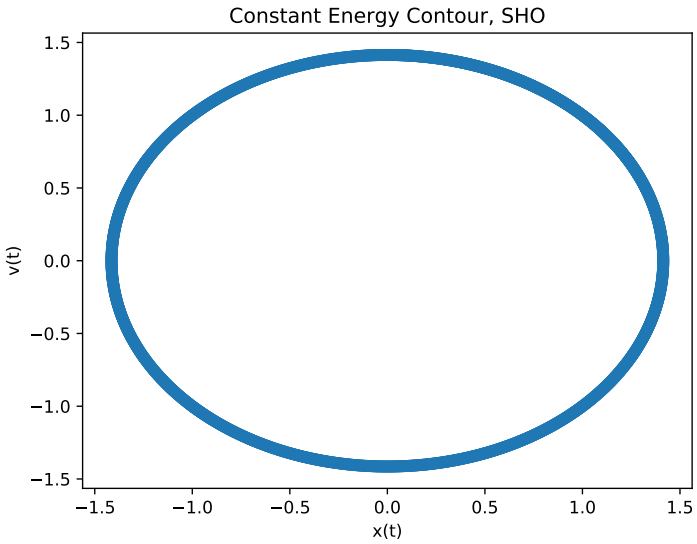
The trajectory produced by the MD simulation for the linear spring is:



The fact that is impossible to tell this apart from the analytical solution is a good thing: i.e. the MD trajectory matches the analytical trajectory very well.

The position on the potential energy surface for the given initial conditions and the phase space trajectory are:



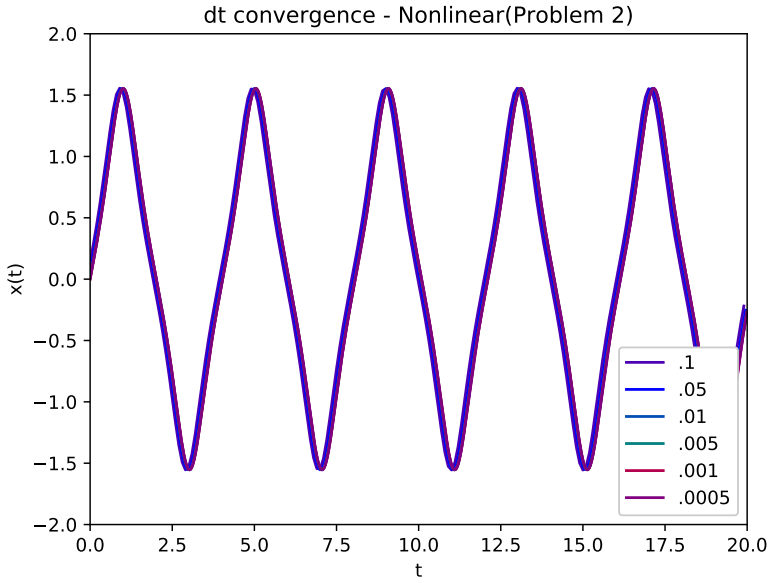


The position oscillation sinusoidally from 1.414 to -1.414 which is in agreement with the total energy available to the particle; the phase space plot agrees with this observation and also shows that the velocity oscillates between -1.414 and 1.414. The elliptical shape of the phase space plot matches what is expected for a SHO.

Part (d):

Using the same MD code with a different function to calculate the forces (both fx's can be found in the 'problem2fx.py' script), I ran the MD simulation for the nonlinear spring.

I used the same time-step. I decided on the time step the same way: by checking the convergence:

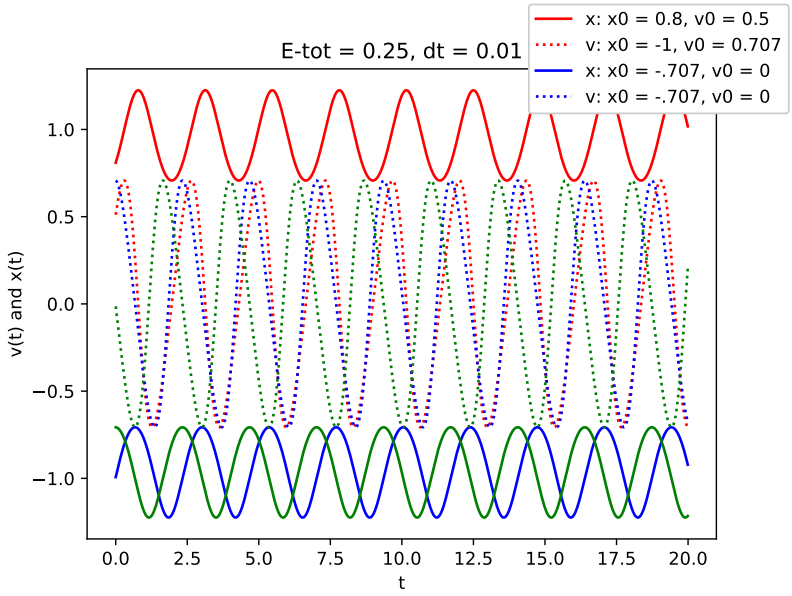


Note that I didn't check for dt > 0.1. My simulation was unstable and blew up for these trajectories. I picked 0.01 again for the same reason as the linear spring.

For each energy, I considered 3 initial conditions: KE = PE, KE = E and PE = 0,

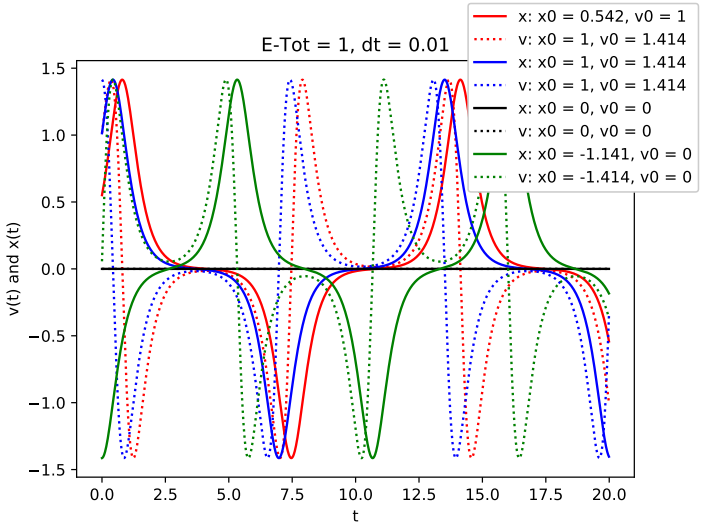
PE = E and KE = 0. i.e. equal parts kinetic and potential, all kinetic, and all potential.

For the case of E = 0.25, the trajectory is confined into one of the wells, as can be noted in the figure below. The only difference in any case is where the initial position is, i.e. which well the particle is stuck in.



The positions are solid lines, the velocities are dotted for reference. Note that the positions for any initial conditions are confined to one of the wells.

For E = 1, i.e. the height of the barrier in the middle of the well, the particle has a turning point at the top of the top of the barrier; however, for KE = 0 and the particle sitting on top of the barrier, the particle never moves. This is expected as the top of the barrier is an extrema in the potential; i.e. a particle here will experience no force (due to the potential).



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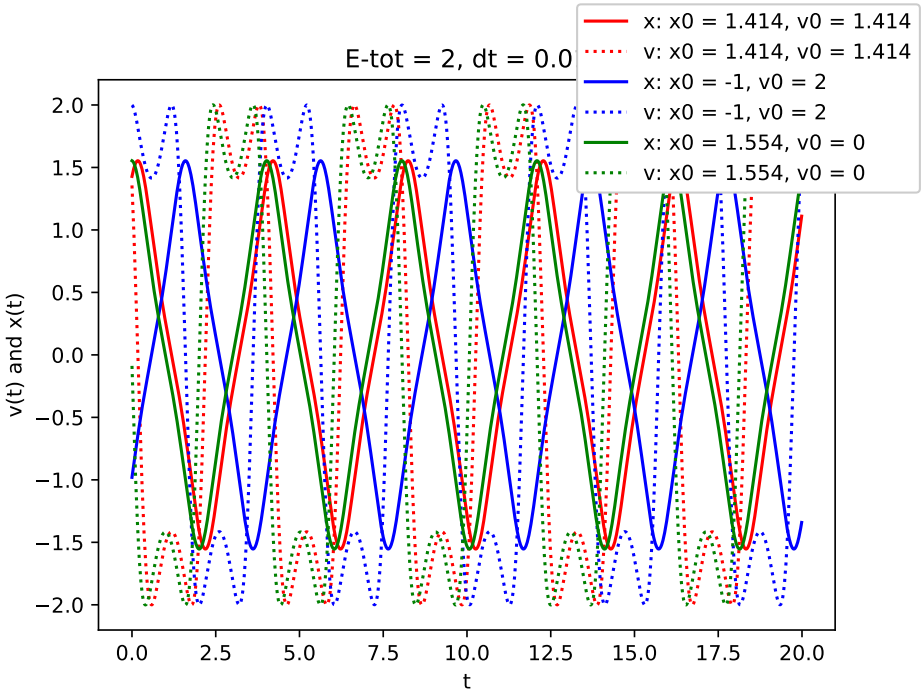
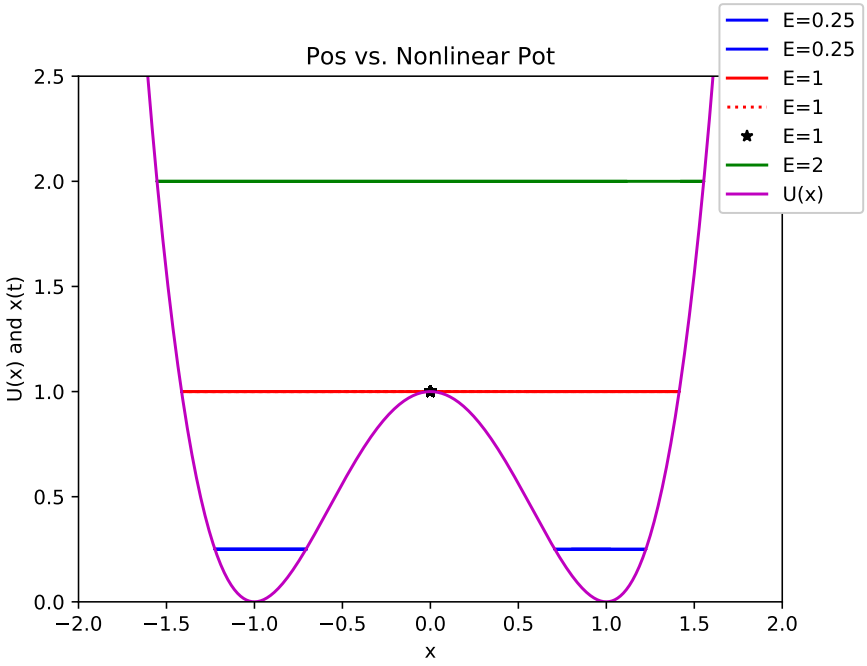
For KE > 0 or the particle initially not at the center, the whole well is accessible to the particle. If the particle is at the center of the barrier with KE = 0, it never moves (the black line). I am guessing the particle doesn't actually turn around at the top due to numerical inaccuracies in the simulation; in HW 2, we showed that the center of the barrier IS a turning point.

For E = 2, the initial conditions aren't important. The particle can traverse the whole well.



For any initial conditions, the particle follows the same trajectory (offset by a phase factor)

For each of the initial conditions above, here is the position of the particle superposed onto the potential energy surface.



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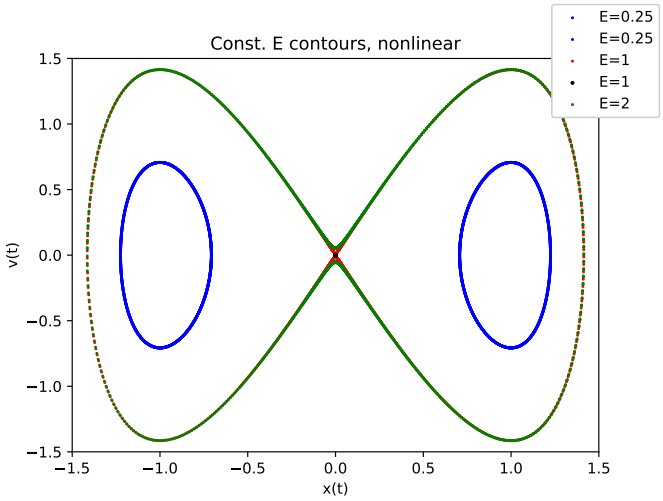
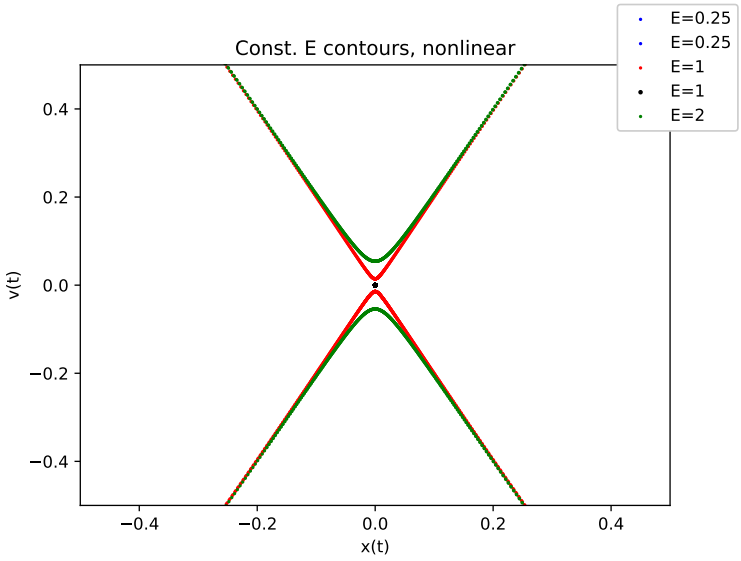
In agreement with the plots of x(t), for E = 0.25 the particle is stuck in one of the wells. For E =1, the particle can travel the whole well EXCEPT when the particle is sitting psuedostabilly at the top of the barrier. When the particle has E = 2, it can travel anywhere.

The phase space plots agree with the plots of v(t) and x(t) as well as the plot superposed on the energy surface.





For the case of E = 0.25, we can see that the particle is stuck in one of the wells (the blue curve). When E = 1, the particle can traverse one of the whole wells with a turning point at the top. When the particle is initially sitting still at the top, it remains there (black). For E = 2, the particle can access the whole well (green).

$$\vec{f}_{LJ} \rightarrow \dot{\vec{p}} = -\frac{\partial H}{\partial \vec{r}} = -\frac{\partial U}{\partial \vec{r}}$$

For $U \rightarrow U^{LJ}$

$$\dot{\vec{p}}_i = \vec{f}_i = -\sum_j \frac{\partial U^{LJ}}{\partial \vec{r}_{ij}} = -\sum_j 4\epsilon \left[\sigma^{12} \frac{\partial |r_{ij}|^{-12}}{\partial \vec{r}_{ij}} - \sigma^6 \frac{\partial |r_{ij}|^{-6}}{\partial \vec{r}_{ij}} \right]$$

$$|r_{ij}| = \left(r_{ij}^{x\,2} + r_{ij}^{y\,2} + r_{ij}^{z\,2}\right)^{\frac{1}{2}}$$

$$\rightarrow \frac{\partial |r_{ij}|^{-12}}{\partial \vec{r}_{ij}} = \frac{\partial \left[\left(r_{ij}^{x\,2} + r_{ij}^{y\,2} + r_{ij}^{z\,2}\right)^{\frac{1}{2}} \right]^{-12}}{\partial \vec{r}_{ij}}$$

$$= \left(\frac{\partial}{\partial r_{ij}^x} \left[|r_{ij}|^{-12} \right] \frac{\partial}{\partial r_{ij}^y} \left[|r_{ij}|^{-12} \right] \cdots \right) = -6 \left(r_{ij}^{x\,2} + r_{ij}^{y\,2} + r_{ij}^{z\,2}\right)^{-7} \cdot 2\, r_{ij}^x \cdots$$

$$= \frac{-12\, r_{ij}^x}{|r_{ij}|^{14}} \cdots = -\frac{12}{|r_{ij}|^2} \cdot \frac{1}{|r_{ij}|^{12}} \cdot \vec{r}_{ij}$$

$$\frac{\partial |r_{ij}|^{-6}}{\partial \vec{r}_{ij}} \rightarrow \frac{-6 \cdot \vec{r}_{ij}}{|r_{ij}|^2 \, |r_{ij}|^6} \rightarrow \vec{f}_{ij} = -\sum_j 4\epsilon \left[\sigma^{12} \left(\frac{-12\, \vec{r}_{ij}}{|r_{ij}|^2 |r_{ij}|^{12}} \right) - \sigma^6 \left(\frac{-6\, \vec{r}_{ij}}{|r_{ij}|^2 |r_{ij}|^6} \right) \right]$$

$$\vec{f}_{ij} = \sum_j \frac{48\epsilon}{|r_{ij}|^2} \left[\left(\frac{\sigma}{|r_{ij}|} \right)^{12} - \frac{1}{2} \left(\frac{\sigma}{|r_{ij}|} \right)^6 \right] \vec{r}_{ij}$$

$$\rightarrow \vec{f}_{ij} = \frac{48\epsilon}{|r_{ij}|^2} \left[\left(\frac{\sigma}{|r_{ij}|} \right)^{12} - \frac{1}{2} \left(\frac{\sigma}{|r_{ij}|} \right)^6 \right] \vec{r}_{ij} \rightarrow \text{NON DIM. } |r_{ij}^*| = \frac{|r_{ij}|}{\sigma}$$

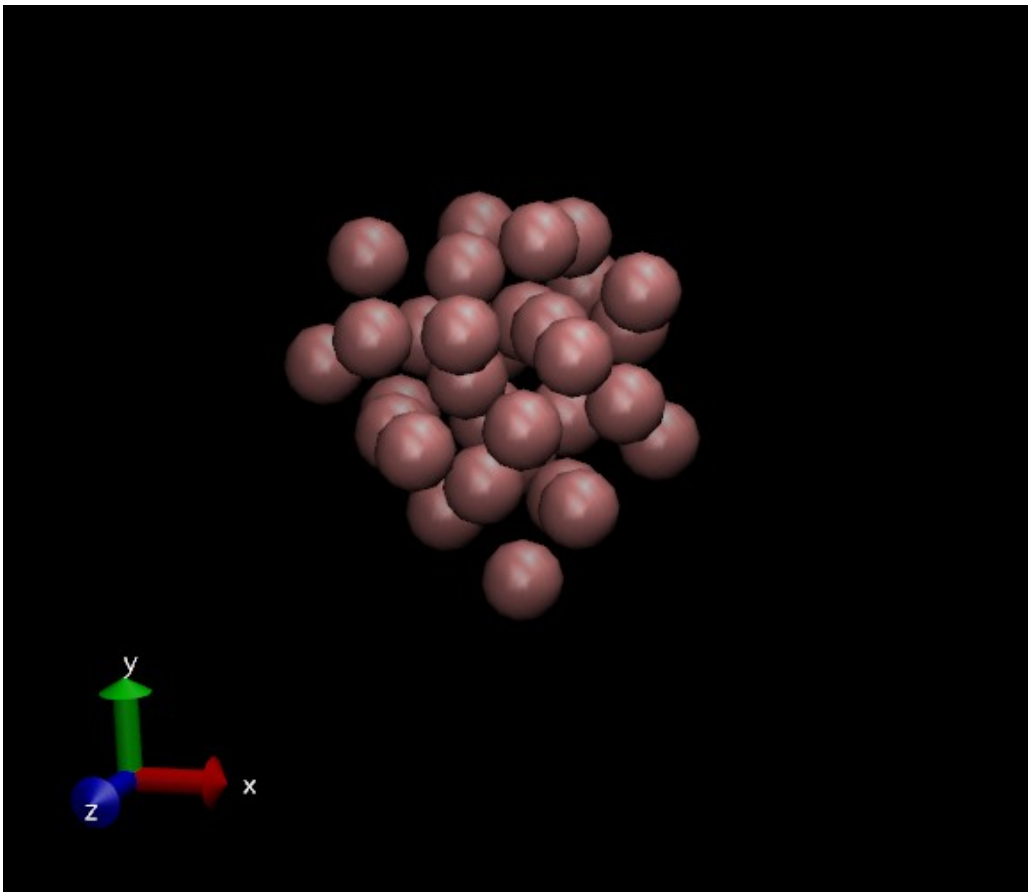
$$\vec{f}_{ij}^{\,*} = \frac{48}{|r_{ij}^*|^2} \left[\left(\frac{1}{|r_{ij}^*|} \right)^{12} - \frac{1}{2} \left(\frac{1}{|r_{ij}^*|} \right)^6 \right] \vec{r}_{ij}$$

SCALAR

VECTOR

$\hookrightarrow \equiv f$

$$\vec{f}_{ij}^{\,*} = \left(r_{ij}^x \cdot f \quad r_{ij}^y \cdot f \quad r_{ij}^z \cdot f \right)$$



Here is a snap shot of the cluster taken at the middle of the simulation.

Notes on my code: In the zip folder in the problem3 directory, you'll find the file 'mainFunctionProblem3.py'

This is the main function that calls all of my other functions from 'moduleMD.py'

I tried to comment both of these quite well, but they're still very complicated.

In my mainFunctionProblem3.py script, all the user has to do is to change the parameters at the top:

infile is the name of the xyz file to read positions from.

dump is the frequency (in steps) that trajectory is written to 'traj.xyz'

thermo is the frequency (in steps) that potential, kinetic, and total energy are written to 'log.MD'

elem = 'argon' in this case; this tells the code what LJ parameters to use.

Nondim = 'argon' in this case; this tells the code what LJ parameters to use to NONDIMENSIONALIZE the data

dist = 'constant' is the velocity distribution; it only supports this now and will raise an error if changed to something else.

Val = 0 is the initial velocity (will also be the seed integer for random sampling)

dt is the time step

tTot is the total simulation time.

you can verify that my codes works correctly by checking the trajectory and the total energy in log.MD. Both are as they should be; i.e. total energy does NOT change over the course of the simulation.

BONUS PART:

Note: I am lazy, so I made the 10 atom cluster by randomly deleting atoms from your input file.

The code runs and behaved exactly as expected; by that, I mean it is not very stable and a few atoms gradually fly away. I am quite confident this is not an error in my simulation as it works for the other cluster and produces the expected vibrations in a 3-atom cluster (equilateral). You can also check the log.MD file in the bonus directory to see that total energy is, in fact, conserved. Just by looking at the vmd video, total momentum appears conserved.