1. The Lennard-Jones potential

In class we heard that any potential can be approximated near its minimum by a harmonic oscillator potential. In this problem we use the Lennard-Jones potential, a popular interparticle potential in molecular physics, as an example. The Lennard-Jones potential is given by

\[ U(r) = 4\epsilon \left[ \left( \frac{r}{\sigma} \right)^{-12} - \left( \frac{r}{\sigma} \right)^{-6} \right], \tag{1} \]

where \( r \) with \( 0 < r < \infty \), is the distance between the two interacting particles, \( \epsilon \) is an energy that describes the depth of the potential, and \( \sigma \) is a length that describes the range of the potential. The values of the parameters \( \epsilon \) and \( \sigma \) depend on the material. For example, the values for argon are \( \epsilon = 1.656 \times 10^{-21} \text{ J} \) and \( \sigma = 3.405 \times 10^{-10} \text{ m} \). The mass of an argon atom is \( m_{\text{Argon}} = 6.63 \times 10^{-26} \text{ kg} \).

(a) On paper:

In mechanics, we typically work in SI units, that is with meter for length, kilogram for mass, second for time and Joules for energy. Please note that only three of these four units are independent since \( 1\text{J} = 1\text{kg} \cdot \text{m}^2/\text{s}^2 \). In problems involving interparticle potentials, SI units are not convenient. Instead, one chooses \( \epsilon \) as the unit for energy, \( \sigma \) as the unit for length, and the mass of the particle as the unit for mass. This choice fixes the unit for time. Write an equation for the unit of time in terms of the Lennard-Jones parameters and the mass of the particle, then evaluate this time unit using the parameters for argon to determine the value of the time unit in seconds.

(b) Write a small Matlab program to plot the potential \( U(r) \) as a function of \( r \) for values of \( r \) between \( 0.5\sigma \) and \( 3\sigma \). Set limits on the energy axis that allow you to see the shape of the potential, from \(-1.5\epsilon\) to \(+3.0\epsilon\) is a good choice. From your graph, determine the distance \( r_{eq} \), where the potential has its
minimum, and determine the minimum value $U_{eq} = U(r_{eq})$ of the potential. Please note: to calculate in units of $\epsilon$ and $\sigma$, all you have to do is set $\epsilon = 1$ and $\sigma = 1$ in your Matlab file.

(c) On paper: Use calculus to find the minimum of the potential, i.e. the distance $r_{eq}$ and the value $U(r_{eq})$. Compare with your result from the graph and resolve any discrepancies. Hint: you should find $r_{eq} = 2^{1/6}$.

(d) On paper: Perform a Taylor expansion to second order of the potential $U(r)$ about $r_{eq}$. Then compare your result with

$$U_{\text{harmonic}} = U_{eq} + \frac{1}{2} k(r - r_{eq})^2,$$

(2)

to determine the value of the “spring constant” $k$.

In Matlab: Add a plot of $U_{\text{harmonic}}$ to your graph of the Lennard-Jones potential and make sure that the potentials agree near the minimum. If not, recalculate your value for $k$.

2. Particle moving in a Lennard-Jones potential

(a) On paper: We discussed in class that we can calculate the force corresponding to a potential from the negative gradient of the potential. For the Lennard-Jones potential, which depends only on the distance $r$, calculate the force from

$$F(r) = - \frac{dU}{dr}.$$

(3)

Now use Newton’s second law to write down the equation of motion, i.e. the second-order differential equation whose solution $r(t)$ is the trajectory of the particle. Then transform it into two first order differential equations for the Matlab ODE solver.

(b) Write a program that determines the motion of a particle in the Lennard-Jones potential; remember, in LJ units, $m = 1$. Please include a plot for the position as a function of time and a phase space plot. Please do not set axis limits until you have a good idea what is going on.

First choose initial conditions that correspond to the bottom of potential,

$$r(0) = 1.01r_{eq} \quad \text{and} \quad v(0) = 0.0$$

(4)

and calculate the trajectory for a time interval between 0 and 3.0 (in LJ time units). You should find (essentially) simple harmonic motion about $r_{eq}$ with a frequency of $\omega_{\text{nat}} = \sqrt{k/m}$, where $k$ is the value of the “spring constant” you determined in 1.(d).

(c) Keeping the initial value for $r(0)$, change the value of the initial velocity first to $v(0) = 0.5$, then $v(0) = 1.0$, and finally $v(0) = 1.5$. For the four initial conditions, compare the graphs for the position as a function of time with each other and compare the phase space plots with each other. Physically, what is going on for $v(0) = 1.5$?