

Final project Atomic interactions

1 Introduction

In this project we model in MATLAB the binding between atoms. We first model the interaction between two atoms in a mutual Lennard-Jones potential and make a harmonic approximation to the potential close to the equilibrium. Second, we model the atomic motion in a triatomic molecule. Finally, we investigate the vibrations in a linear chain of atoms.

2 Instruction

Make a complete .m file that addresses all tasks (1 to 6) of this project. In the oral examination you have to demonstrate the answers to all tasks by running your MATLAB code. Make sure that you can run the code and subsections of the code. Put the graphs for every task in a single figure using the `figure` and if necessary the `subplot` command. Implement the good programming practices of vectorization, commenting, use of parameters, and use of loops in your code.

3 Atomic interactions

The bonding between two atoms is described by quantum mechanics. However, a classical description of the interaction can be made that gives insight into the bonding mechanism. As an example we consider closed shell atoms such as noble gases. These atoms do not have a permanent dipole moment, i.e., they are electrically neutral. Therefore direct Coulomb interaction between these atoms does not play a role. However, in these atoms there are mutually induced dipoles that are caused by slight misalignment between the positive core and the negative electron cloud. As a result neutral atoms attract each other via dipole-dipole interaction.

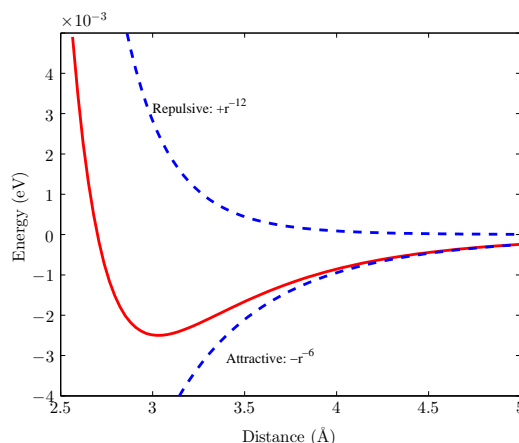


Figure 1: Lennard-Jones potential showing the attractive and repulsive contributions.

The dipole-dipole interactions result in an attractive force that acts mainly at a long distances r and has an r^{-6} dependence. When the atoms are close together their electron clouds start to overlap and the atoms feel a strong (Coulomb) repulsion that has an r^{-12} dependence. The total interaction potential is commonly described by the so-called Lennard-Jones (LJ) potential, which contains both the attractive and repulsive contribution to the interaction. The Lennard-Jones potential is described as:

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

with ε the interaction energy and σ the separation at which the potential is zero. A schematic overview of the LJ potential of Eq. 1 is shown in Fig. 1.

Task 1

The file `ljdata.mat` contains measurements of a Lennard-Jones potential, albeit with some experimental noise. Download the file `ljdata.mat` to your computer and load the variables into MATLAB using the `load` command. The file contains three variables: the first column `r` is the distance in meters, the second column `potr` is the measured potential energy in Joules, and the third column `noisepotr` is the standard deviation for every measurement in Joules.

- (a) Fit the LJ potential of Eq. 1 to the experimental data. Use the generalized least squares including measurement error that you learned in project 5 for this. What are the fitted ε and σ ? Plot in a first subplot the experimental data with errorbars and overlay the LJ fit. Create the LJ fit data using a MATLAB function with a vector of distances, ε , and σ as input. Use $N=100$ points equidistantly spaced between the smallest and largest distance of the measured data to create your distance axis.
- (b) Determine the equilibrium point r_{equi} of the potential $V(r)$, i.e., determine the point where the derivative of the potential is zero. Do this analytically, i.e., with pen and paper.
- (c) Fit a harmonic oscillator potential around the equilibrium position of **1(b)** to the LJ potential that you fitted in **1(a)**. Base your parabolic fit on a range of points of your fitted LJ potential function around equilibrium and use the generalized least square method with the function $P(r) = P_0 + \frac{1}{2}k_s(r - r_{\text{equi}})^2$ as your parabolic fit function. The parameter r_{equi} is not a fit parameter, but the analytically determined equilibrium position. You can use the generalized fit method from project 5, but take into account that the fitted points now have zero uncertainty. For what range around the equilibrium point do you still get a good parabolic fit?

Plot the parabolic fit in the graph of **1(a)** in a first subplot and make a second subplot of the same data, but zoomed in on the region around the equilibrium.

- (d) Calculate the derivative of both the LJ-potential and the harmonic potential with pen and paper and determine the force $F(r)$ on a particle in the potential using $F(r) = -dV/dr$. Make a vector based MATLAB function to calculate the force with the position as input. Plot the force $F(r)$ acting on a particle in a third and fourth

subplot. Draw the graphs in the same distance range as the corresponding potential plots and make sure to use the correct units.

- (e) Expand $V(r)$ of Eq. 1 in a Taylor series around the equilibrium position to quadratic order using pen and paper and find an expression for the spring constant k_s of the harmonic oscillator approximation to $V(r)$. Compare the spring constant you obtain from the Taylor expansion to the value you get from the parabolic fit. Vary the fit range for your parabola to make sure that the spring constant from your parabolic fit is close to the analytical expression for the spring constant.

The motion of the hydrogen molecule can be modeled using either the fitted Lennard-Jones potential or the fitted harmonic potential approximation. However, the motion of a single particle in a potential of a second particle is a complicated two-body problem. The interaction forces are in the direction along the line joining the two particles. In general, we are interested in the relative motion of the particles with respect to each other. By replacing the particles' mass with the so-called effective mass $m_{\text{eff}} = m_1 m_2 / (m_1 + m_2)$ this problem can be reduced to a one-body problem. For example, the acceleration of particle 1 relative to particle 2 is given by $F_{12} = m_{\text{eff}} a_{\text{rel}}$. So the replacement of the mass with the reduced mass leads to the two-body problem to be reduced to a one-body problem. The hydrogen atom has a mass of 1 atomic mass unit (1 amu = $1.67 \cdot 10^{-27}$ kg), hence, for molecular hydrogen (H_2) the reduced mass is 0.5 amu. In the model it is assumed that there are no thermal effects, i.e., the simulation is performed for a temperature of 0 K.

Task 2

- (a) Model the motion of two hydrogen atoms in the mutual LJ-potential as given by Eq. 1 using the previously fitted values for ϵ and σ . Calculate the force from the potential and solve the equation of motion using the MATLAB `ode45` solver with 500 points equidistantly spaced in the interval $t \in [0, 1 \cdot 10^{-14}]$ seconds (look in project 6 for more details on how to do this). Perform the same analysis for the harmonic oscillator approximation close to the equilibrium. Plot the position of the atom in the LJ and harmonic oscillator in a first subplot and its velocity in a second subplot.
- (b) Calculate the speed from the simulated motion $x(t)$ for both the LJ and harmonic potential using a numerical differentiation of the position $x(t)$ based on the two-point center difference approximation. Use vectorized code for calculating the velocity. Compare your results to the velocity you get from the `ode45` solver by plotting that solution in the same subplot.
- (c) Calculate a numerical approximation of the second order derivative $f''(x)$ based on the application of the forward difference. Determine for both the LJ and the harmonic potential the acceleration from the position $x(t)$ using this second order derivative. Use vectorized code for calculating the acceleration and make sure that the units are correct. Plot the acceleration for the LJ potential and the harmonic oscillator approximation in a third subplot.

- (d) Vary the initial starting position of the particle. Start close to equilibrium position and gradually move away. Explain the different behavior of the particle in both the LJ and harmonic potential.

4 Intramolecular vibrations

We have seen that the binding potential of atoms in a molecule can be approximated by a harmonic oscillator potential. The connections between the molecules can be considered as little springs with the force proportional, but opposite in direction to, the displacement. We use this simplified model to calculate the vibrational modes of CO_2 . A further simplification is to consider the three atoms to be aligned and the atoms only vibrate along the line connecting the atoms, as indicated in Fig. 2.

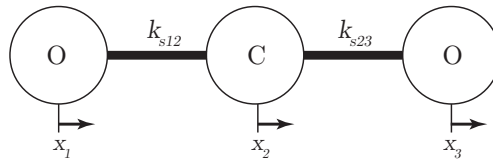


Figure 2: Schematic of the CO_2 molecule.

Assuming that only nearest neighbors atoms have an interaction (i.e., $k_{s13} = 0$), the equations of motion for the three atoms are given by combining Newtons' second law with Hooks' law and result in

$$\begin{aligned} m_1 x_1'' &= -k_{s12}(x_1 - x_2) \text{ left atom} \\ m_2 x_2'' &= -k_{s12}(x_2 - x_1) + k_{s23}(x_3 - x_2) \text{ middle atom} \\ m_3 x_3'' &= -k_{s23}(x_3 - x_2) \text{ right atom,} \end{aligned} \quad (2)$$

with the positions x_n defined relative to the center coordinate of each atom. For the CO_2 molecule we can use the following notations $k_{s12} = k_{s23} = k_s$, $m_1 = m_3 = m_O$, and $m_2 = m_C$. The equations of motion become

$$\begin{aligned} m_O x_1'' &= -k_s(x_1 - x_2) \\ m_C x_2'' &= -k_s(x_2 - x_1) + k_s(x_3 - x_2) \\ m_O x_3'' &= -k_s(x_3 - x_2), \end{aligned} \quad (3)$$

As the vibrations are expected to be harmonic functions we use as a trial solution $x_n = x_{n0} \cos \omega t$, with ω the angular frequency and $n=1,2$, or 3 indicating the position of the atoms. Inserting this solution into Eq. 3, a linear system of equations is found describing the motion of the atoms.

Task 3

- (a) Compute an analytical expression for the solution of Eq. 3 using pen and paper. Find the frequencies of the solutions for the particle motion described by $x_n = x_{n0} \cos \omega t$

using substitution. First solve the frequencies for the case where $x_{20} = 0$ and second for the case where $x_{20} \neq 0$. Second, find the amplitudes x_{n0} for all the modes by re-substitution of the harmonic solutions $x_n = x_{n0} \cos \omega t$ in the equations of motion, Eq. 3 for the frequencies that you found.

- (b) Use the carbon (12 amu) and oxygen (16 amu) mass in combination with a spring constant of $k_s = 1500$ N/m to calculate in MATLAB the frequencies of the vibrational modes based on the obtained analytical formulas in **3(a)**.

An alternative way to solve the time dependent solution of this system of equations is using the ode functions from MATLAB. In this case we have to use the state representation $y = [x_1 \ x'_1 \ x_2 \ x'_2 \ x_3 \ x'_3]^T$ of the positions and velocities of the three atoms. The equations of motion for this state representation can be written in matrix notation as

$$y' = A y. \quad (4)$$

With the appropriate starting conditions the frequency of the solution can be determined from the time dependence of the positions.

Task 4

- (a) Model the motion of the CO₂ molecule in the harmonic approximation for $t \in [0, 1 \cdot 10^{-13}]$ seconds using the `ode45` function. Determine the matrix A and use the starting conditions you determined in **3(a)** with $x_{10}=1$. Plot the solutions x_1 , x_2 , and x_3 for the two fundamental modes in two separate subplots.
- (b) Can you observe the modes of the vibrating molecule, to what molecular motion do the modes correspond to? Chemists denote spectroscopic frequencies as wavenumber in units cm^{-1} . For CO₂ the low frequency mode is at $\tilde{\nu}_1 = 1340 \text{ cm}^{-1}$ and the high frequency mode is at $\tilde{\nu}_2 = 2349 \text{ cm}^{-1}$. Check that the frequencies you got match the answer of task **3(b)** and that they correspond to the frequencies ν_1 and ν_2 . Use $c = \lambda \nu$ for the conversion between frequency in Hz and cm^{-1} .

5 Vibrations in a mono-atomic linear solid

The harmonic oscillator is also a good model to simulate atomic motion in a solid. Consider the linear chain of N atoms of mass m and lattice spacing a as shown in Fig. 3.

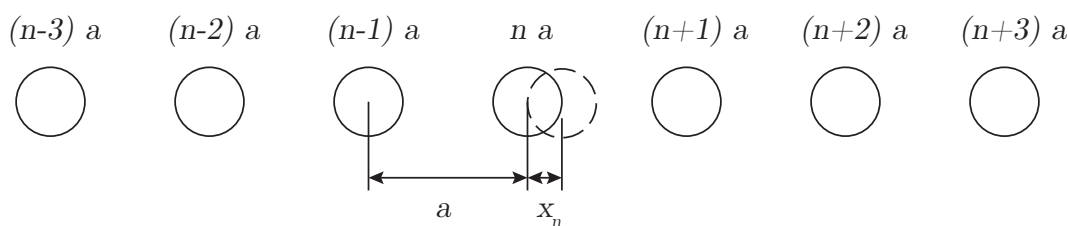


Figure 3: A linear chain of atoms.

Using a formalism similar to that for the molecular interaction we assume that only nearest neighbors influence each other via a harmonic potential. Hence for every particle in the chain we can write

$$mx_n'' = k_s(x_{n+1} - 2x_n + x_{n-1}), \quad (5)$$

with n running from 1 to N . We look for solutions x_n that have a harmonic time dependence as

$$x_n(t) = x_{n0} \cos \omega t, \quad (6)$$

with ω the angular frequency. Moreover, we consider periodic boundary conditions for the atoms at the beginning and the end of the chain, which we assume to be identical. Hence, for the atom at the beginning of the chain it holds that $mx_1'' = k_s(x_2 - 2x_1 + x_N)$ and the end of the chain it holds that $mx_N'' = k_s(x_1 - 2x_N + x_{N-1})$.

Task 5

- Use Eq. 6 in Eq. 5 and write down with pen and paper the eigenvalue equation describing the motion for all particles in the chain x_n .
- Set up the matrix for the equations of motion for a linear chain consisting of $N=41$ particles of mass $m=1$, and spring constant $k_s = 9$. Use vectorization to fill up the matrix.
- Determine the eigenvalues and eigenvectors for your 41×41 matrix using MATLAB. Note that you get $(N-1)/2$ eigenvalues twice (these ω_n are called degenerate) and the trivial solution $\omega = 0$, which is present only once. Plot the solution $x_n(t)$ for the first five unique eigenvectors as a function of particle position na for $t = 0$ in a first subplot.

Apparently the initial position of the particles has a sinusoidal form. The sinusoidal initial displacement can be described by its period λ and its wavenumber $k = 2\pi/\lambda$. Because of the periodic boundary conditions there are $(N-1)/2 + 1$ unique frequencies ω_n related to the integers $n = 0, \pm 1, \pm 2, \dots, \pm(N-1)/2$.

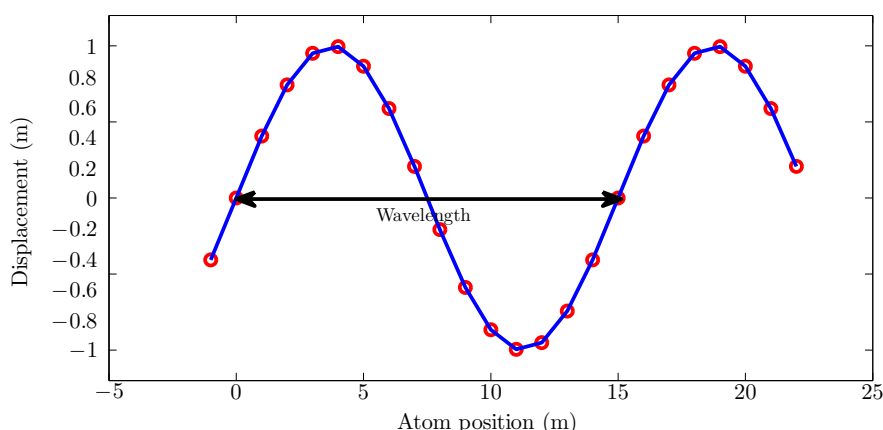


Figure 4: Displacement of the atoms as a function of position.

Task 6

- (a) From the plot of the displacements, determine a relation for the wavelength for every mode in terms of the mode number n , the chain length N and the period a as demonstrated in Fig. 4. Calculate the wavenumber from the wavelength.

In solid state physics it is derived that the relation between frequency and wavenumber is given by

$$\omega = \sqrt{\frac{2k_s(1 - \cos(ka))}{m}}. \quad (7)$$

- (b) Plot the frequency ω_n of the mode versus its wavenumber k in a second subplot for all the frequencies calculated in task 5(c) (you have to sort the frequencies in an appropriate way to the linear wavenumber). This plot is known as a dispersion relation. Add the theoretical functional dependence of Eq. 7 to your graph.

In this project we have shown that two interacting atoms can be described by a single oscillation frequency and periodic motion. For a tri-atomic molecule there are multiple oscillation frequencies and the atoms have their individual, although coupled, periodic motion. For a linear chain of particles the motion of all individual particles is coupled and described by a large number of frequencies.