E1 Coupled harmonic oscillators

Oscillatory motion is common in physics. Here we will consider coupled harmonic oscillators. Fourier transformation of the time-dependence can be used to reveal the vibrational character of the motion and normal modes provide the conceptual framework for understanding the oscillatory motion.

You will first study the motion of the triatomic linear molecule carbon dioxide. You will model the bonds between the atoms as harmonic oscillators and you will solve Newton's equations of motion using the velocity Verlet algorithm. Then you will consider the Fermi-Pasta-Ulam-Tsingou problem, or formely the Fermi-Pasta-Ulam problem. It was one of the first non-trivial problems that was studied using computers. Fermi and coworkers wanted to check the predictions of statistical mechanics on the thermalization of solids.

This task is paired with code questions in Yata that are mandatory to pass before being allowed to present. You should solve the problems using the `C` language and the Yata questions will help you verify that your code is correct.

1 Coupled harmonic oscillators

Consider three harmonically coupled particles. The masses of each particle are m_1, m_2 and m_3 and the springs are identical with a spring constant κ. We denote the displacements from the equilibrium positions with q_i, i=1,2,3 and v_i for the corresponding velocities.

Figure 1: System of three coupled harmonic oscillators with free boundary conditions.

The Hamiltonian for the system is given by

$$\mathcal{H} = \sum_{i=1}^{3} \frac{m_i v_i^2}{2} + \sum_{i=1}^{2} \frac{\kappa}{2}(q_{i+1} - q_i)^2$$

and the corresponding equations of motion can be written as

$$\begin{aligned} m_1 \ddot{q_1}(t) &= \kappa\left[q_2(t) - q_1(t)\right] \\ m_2 \ddot{q_2}(t) &= \kappa\left[q_3(t) - 2q_2(t) + q_1(t)\right] \\ m_3 \ddot{q_3}(t) &= \kappa\left[-q_3(t) + q_2(t)\right], \end{aligned}$$

where the double dots denote a second time derivative. This is a set of three coupled second order ordinary differential equations. These can be solved

using a stepping procedure in time. One popular method is the velocity Verlet algorithm

$$q_i(t+\Delta t) = q_i(t) + v_i(t)\Delta t + \frac{1}{2}a_i(t)\Delta t^2$$
$$v_i(t+\Delta t) = v_i(t) + \frac{1}{2}[a_i(t) + a_i(t+\Delta t)]\Delta t$$

where Δt is the timestep and $a_i = \ddot{q}_i$ is the acceleration for particle i. In this case we have

$$a_i(t) = \frac{\kappa}{m}\,[q_{i+1}(t) - 2q_i(t) + q_{i-1}(t)]$$

One step in the velocity Verlet algorithm can be coded in an efficient way as

$$v_i(t+\Delta t/2) = v_i(t) + \frac{1}{2}a_i(t)\Delta t$$
$$q_i(t+\Delta t) = q_i(t) + v_i(t+\Delta t/2)\Delta t$$
`calculate new accelerations/forces`
$$v_i(t+\Delta t) = v_i(t+\Delta t/2) + \frac{1}{2}a_i(t+\Delta t)\Delta t$$

which only requires the storage of positions and velocities at one time point.

Task

1. Consider the motion of the molecule CO_2. Regard the system as three particles bound with springs, with free boundary conditions (see Fig. 1). Consider the motion only in one dimension. The spring constant for carbon dioxide is $\kappa = 1.6\,\mathrm{kN/m}$.

   Answer the questions for **E1 task 1** on Yata to verify that you correctly convert the necessary input parameters to the Atomic Simulation Units. These units are described in the appendix to this document.

2. Do **E1 task 2** on Yata, where you implement the velocity Verlet algorithm for CO_2 in one dimension.

3. Write a program on your computer using the code that you have verified on Yata. The program should numerically solve the equations of motion using the velocity Verlet algorithm. Assume the initial condition $q_1(0) = 0.01$ Å, $q_2(0) = 0.005$ Å and $q_3(0) = -0.005$ Å. Set all initial velocities to zero, $v_1(0) = v_2(0) = v_3(0) = 0$. Plot your result, like in Figure 2. Determine also the time-dependence of the potential, kinetic and total energies (Figure 3). Do you conserve total energy? Vary the time-step and investigate the energy conservation. (1 p)

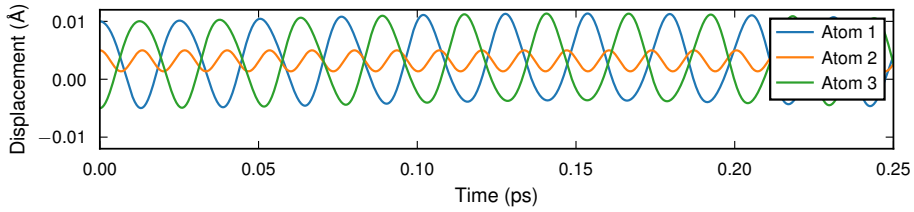

Figure 2: The time-dependent displacements for the CO_2 molecule.

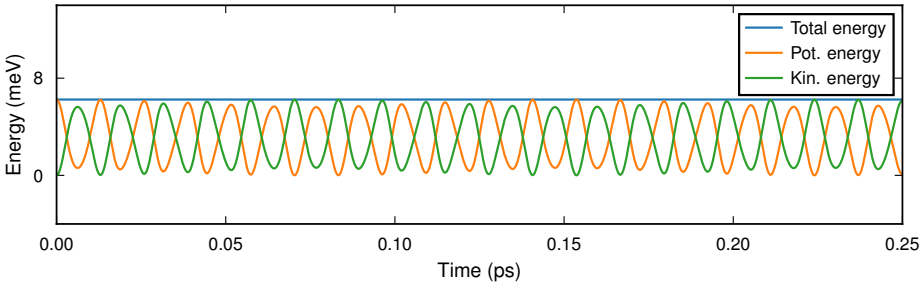

Figure 3: The time-dependence of the potential and kinetic energies for the CO_2 molecule.

4. Choose an appropriate time-step Δt based on conservation of the total energy. Compute the powerspectrum and try to determine the normal mode frequencies. Fill in the answers in **E1 task 4** on Yata. Compare with the experimental data for CO_2. (1 p)

2 The Fermi-Pasta-Ulam-Tsingou problem

After the second world war Enrico Fermi and coworkers at Los Alamos became interested in using the newly developed computing machines to test physical ideas, to perform *computer experiments* or *computer simulations*. They wanted to check the prediction of statistical mechanics on the thermalization of solids, which relies on the ergodic hypothesis. Fermi, Pasta, Ulam and Mary Tsingou [1] considered a vibrating string that included a non-linear term. To their surprise they found that the behavior of the system was quite different from what intuition would have led them to expect. Fermi thought that after many iterations, the system would exhibit thermalization, an ergodic behavior in which the influence of the initial modes of vibration fade and the system becomes more or less random with all modes excited more or less equally. Instead, the system exhibited a very complicated quasi-periodic behavior [2].

The *Fermi-Pasta-Ulam-Tsingou* (FPUT) experiment was important both

in showing the complexity of nonlinear system behavior and the value of computer simulation in analyzing systems. It is also central in the theory of solitons. When considering the FPUT problem Zabusky and Kruskal [3] were able to explain the the periodic behavior in terms of the dynamics of localized excitations. They introduced the notion "solitons" for these waves with particle type of properties.

The FPUT model consists of a one-dimensional chain of masses connected with non-linear springs.

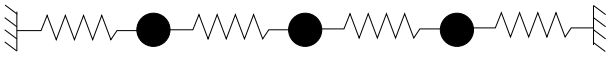

Figure 4: System of three coupled harmonic oscillators with fixed boundary conditions.

The so called α-model is defined by the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=0}^{N} \left[\frac{\kappa}{2}(u_{i+1} - u_i)^2 + \frac{\alpha}{3}(u_{i+1} - u_i)^3 \right]$$

where m is the mass of the particles, u_i the displacement of particle i from its equilibrium position, and p_i the corresponding momentum. The harmonic force constant is denoted by κ and α is a measure of the anharmonic coupling strength. The boundary conditions are $u_0 = u_{N+1} = 0$.

For the Fermi-Pasta-Ulam-Tsingou problem it is convenient to put $m = \kappa = 1$, which then defines the dimensionless units that are used.

Task

5. Derive the corresponding equation of motion for $u_i(t)$. Enter the result in **E1 task 5** in Yata.

6. Implement the equation of motion in **E1 task 6** in Yata.

3 Harmonic case

In the harmonic case, with linear springs only ($\alpha = 0$), the problem can be solved analytically. The solution can then be expressed in terms of *normal modes*, the eigenvectors, according to

$$Q_k = \sqrt{\frac{2}{N+1}} \sum_{i=1}^{N} \sqrt{m} u_i \sin\left(\frac{ik\pi}{N+1}\right), \quad k = 1, \ldots, N$$

$$P_k = \sqrt{\frac{2}{N+1}} \sum_{i=1}^{N} \frac{p_i}{\sqrt{m}} \sin\left(\frac{ik\pi}{N+1}\right), \quad k = 1, \ldots, N$$

where the corresponding eigenfrequencies are given by

$$\omega_k = 2\sqrt{\frac{\kappa}{m}} \sin \frac{k\pi}{2(N+1)} \quad k = 1, \ldots, N$$

The inverse transforms are

$$u_i = \sqrt{\frac{2}{N+1}} \sum_{k=1}^{N} \frac{Q_k}{\sqrt{m}} \sin\left(\frac{ik\pi}{N+1}\right), \quad i = 1, \ldots, N$$

$$p_i = \sqrt{\frac{2}{N+1}} \sum_{k=1}^{N} \sqrt{m} P_k \sin\left(\frac{ik\pi}{N+1}\right), \quad i = 1, \ldots, N$$

The Hamiltonian for the system

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=0}^{N} \frac{\kappa}{2}(u_{i+1} - u_i)^2$$

is then transformed to

$$\mathcal{H} = \sum_{k=1}^{N} E_k = \frac{1}{2} \sum_{k=1}^{N} \left[P_k^2 + \omega_k^2 Q_k^2\right]$$

which shows that the system can be described by N independent modes with energy

$$E_k = \frac{1}{2}\left[P_k^2 + \omega_k^2 Q_k^2\right] \quad k = 1, \ldots, N$$

Task

7. Implement the transformation between the ordinary coordinates u_i and p_i and the normal coordinates Q_k and P_k in **E1 task 7** in Yata.

8. Write a `C` program that solves the equation of motion and determines $u_i(t)$ and $p_i(t)$. Use the code that you have just verified on Yata.

   Consider the harmonic case, $\alpha = 0$. Assume initial conditions $u_i(0)$ and $p_i(0)$ such that that all energy is initially localized in mode $k = 1$, i.e. $E_k(t = 0) = E_0\ \delta_{1k}$, and only kinetic, i.e. $P_k = \sqrt{2E_0}\ \delta_{1k}$ and $Q_k = 0\ \forall k$. Consider the case $N = 32$ and assume $E_0 = N$.

   Perform a simulation with time-step Δt=0.1 for the time span t_{max}=25 000. Plot $E_k(t)$, k=1,2,...,5. Verify that $E_k(t) = E_k(0)$, i.e. no energy transfer takes place among the normal modes. (1 p)

4 Equipartition

The *equipartition theorem* in classical statistical mechanics states the *mean value of each independent quadratic term in the Hamiltonian is equal to* $k_BT/2$, where T is the temperature for the system [4]. This is derived using ensemble averaging. This implies that for the harmonic case above we have

$$\left\langle \frac{1}{2}P_k^2 \right\rangle_{ens} = \left\langle \frac{1}{2}\omega_k^2 Q_k^2 \right\rangle_{ens} = \frac{k_BT}{2} \ , \quad \forall k$$

and that the energy in each mode should be equal

$$\langle E_k \rangle_{ens} = k_BT \ , \quad \forall k$$

The *ergodic hypothesis* states that the ensemble average $\langle \ldots \rangle_{ens}$ and time average $\langle \ldots \rangle_{time}$ are equal and the ensemble average could then be obtained by performing a time average, by computing the time evolution of the system. This is obviously not true for the harmonic system above, the initial distribution of the energy over the different modes will be kept for ever, no equipartition of the energy. It was then believed that any weak anharmonicity would introduce energy transfer between the modes and eventually equipartition the energy. This was precisely what Fermi and coworkers wanted to test using the FPUT model.

5 Anharmonic case

In the non-linear case, $\alpha \neq 0$, with the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=0}^{N} \left[\frac{\kappa}{2}(u_{i+1} - u_i)^2 + \frac{\alpha}{3}(u_{i+1} - u_i)^3 \right]$$

the solution is not known and the use of computer simulations becomes indispensable, as realized by Fermi and coworkers. The Hamiltonian can be transformed using the normal coordinates as

$$\mathcal{H} = \frac{1}{2}\sum_{k=1}^{N} \left[P_k^2 + \omega_k^2 Q_k^2 \right] + \frac{\alpha}{3} \sum_{k,l,m=1}^{N} c_{klm} Q_k Q_l Q_m \omega_k \omega_l \omega_m$$

The total energy is no longer exactly given by the sum of the energies in the different modes. However, Fermi *et al.* argued that for weak anharmonicity one expects to get equipartition of the energy among the different normal modes.

Task

9. Consider now the anharmonic case, $\alpha \neq 0$, and the two cases $\alpha = 0.01$ and $\alpha = 0.1$. Use the same setup as in the previous task and present your results in the same way. In this case you should obtain energy exchange between the different modes. (0.5 p)

10. Consider again the anharmonic case with $\alpha = 0.01$ and $\alpha = 0.1$, but now consider a considerably longer timespan, $t_{max} = 10^6$. In this case it becomes time-consuming to evaluate and save the energy in the various normal modes at each time-step and the output file becomes very large. Modify therefore your program so that the normal mode energies are calculated and saved only once for each 1000 time-steps. Determine the normal mode energies $E_k(t)$ at the corresponding times, i.e. at

$$t_n = 1000\ n\ \Delta t\ , \qquad n = 1, 2, \ldots$$

Compute the time-average of the normal mode energies

$$\langle E_k \rangle_{\text{time}}(t) = \frac{1}{t} \int_0^t dt'\ E_k(t')$$

Plot your results for $\langle E_k \rangle_{\text{time}}(t)$ for all normal modes with logarithmic scale for both axis. Do you obtain equipartition of the energy? (0.5 p)

Despite the fact that more than 60 years have passed since the Fermi-Pasta-Ulam-Tsingou problem was presented, it has not yet been fully understood [5].

References

[1] T. Dauxois, Physics Today **6**, 55 (2008).

[2] E. Fermi, J. Pasta, and S. Ulam, "Studies of Nonlinear Problems". Document LA-1940 (1955).
See also: http://en.wikipedia.org/wiki/Fermi-Pasta-Ulam_problem

[3] N. J. Zabusky and M. D. Kruskal, Phys. Rev. Lett. **15** 240 (1965).

[4] F. Reif, *Fundamental of Statistical and Thermal Physics* (McGraw-Hill, 1965).

[5] M. Onorato, L. Vozella, D. Proment, and Y. Lvov, PNAS **112** 4208 (2015).

A System of units

SI system

The basic units in the SI system for length (L), mass (M), and time (T) are

L: 1 meter (m)
M: 1 kilogram (kg)
T: 1 second (s)

The units for *e.g.* frequency and energy are then derived from these: Hertz ($1\ \mathrm{Hz} = 1\ \mathrm{s}^{-1}$) and Joule ($1\ \mathrm{J} = 1\ \mathrm{kg\,m^2\,s^{-2}}$), respectively, and cannot be chosen independently.

Atomic simulation units

In computational studies it is often convenient to use other system of units, which are more appropriate for the considered length- and time-scales. In atomic scale simulations the following units, "Atomic simulation units", [1] are often used. The starting point is the basic units

L: 1 Ångström (Å)
T: 1 picosecond (ps)
E: 1 electron volt (eV)

The unit for mass (M) can then not be chosen independently but is given by

$$\mathrm{M} = \mathrm{ET^2L^{-2}}$$

or

$$\mathrm{M:}\ \ \mathrm{m_{asu}} = 1\mathrm{eV}\ \frac{(1\mathrm{ps})^2}{(1\mathrm{\AA})^2} = 1.60218 \cdot 10^{-23}\ \mathrm{kg} = 9649\ \mathrm{u}$$

where u=$1.66054 \cdot 10^{-27}$ kg is the atomic mass unit. In these units the mass m of a oxygen atom is

$$m = 15.9994u/\mathrm{m_{asu}} = 1.658 \cdot 10^{-3}$$

[1] see `http://lammps.sandia.gov/doc/units.html`