Finding the Vibrational Frequency of N$_2$ and O$_2$ Molecules

A Computational Report

Background

The aim of this computational experiment is to obtain the vibrational frequency of N$_2$ and O$_2$ molecules. The two atoms within these molecules are simulated as interacting via the Morse potential, which is frequently used to describe the potential of two atoms bonding to create a diatomic molecule. The energy of two particles under the Morse potential, at r_1 and r_2 is given by $U_M = D_e\left\{\left[1 - e^{-\alpha(r_{12}-r_e)}\right]^2 - 1\right\}$. The force on the particle at r_1 is given by $F_1 = 2\alpha D_e\left[1 - e^{-\alpha(r_{12}-r_e)}\right]e^{-\alpha(r_{12}-r_e)}\hat{r}_{12}$, where $\hat{r}_{12}$ is the unit vector in the direction of $r_2 - r_1$. The parameters α, D_e and r_e are dependent on the which atoms are interacting, in this case nitrogen and oxygen.

The movement of the interacting particles has been simulated at each time step using two different time integration algorithms: the symplectic Euler integration scheme

$$\vec{x}(t + \delta t) = \vec{x}(t) + \vec{v}(t)\delta t \qquad \vec{v}(t + \delta t) = \vec{v}(t) + \vec{a}(t + \delta t)\delta t$$

and the velocity Verlet integration scheme,

$$\vec{x}(t + \delta t) = \vec{x}(t) + \vec{v}(t)\delta t + \frac{1}{2}\vec{a}(t)\delta t^2; \qquad \vec{v}(t + \delta t) = \vec{v}(t) + \frac{1}{2}[\vec{a}(t) + \vec{a}(t + \delta t)]\delta t$$

where the accelerations are found using the force divided by the mass of the particle.

Using the positions of the particles at each time step, the two atoms' separation can be plotted with respect to time. This should form an oscillating plot with peaks, and the distance between the peaks gives the time period, T, of the vibrations. From this, the wavenumber $\bar{v} = v/c$ can be found, where $v = 1/T$ is the frequency.

Time-step estimates

The ideal time-step parameter, δt, must be small enough that the simulation will be fairly accurate, and large enough that the simulation will not take an unreasonable amount of time to run.

The simulations were run for an oxygen molecule with a range of different time steps: 0.2, 0.1, 10^{-2}, 10^{-3}, 10^{-4} and 10^{-5}. As the time steps were decreased, the simulated frequencies of the molecules also decreased. In fact, the decrease of the frequencies decreased itself, showing that the simulations provide a result that converges towards a definite value as the time step parameter tends towards zero.

To determine accuracy of a simulation, one can use the energy inaccuracy $\Delta E = max(E) - min(E)$ and the frequency inaccuracy, $(v - v_0)/v_0$. The best possible estimate of our wavenumber, v_0, is taken to be the wavenumber found by the simulation with the smallest step size, since the simulations will converge to the most accurate estimate as $\delta t \to 0$, as explained.

Frequency Inaccuracy of O2 Molecule with Different δt

Above is the plot of the frequency inaccuracies of the simulations with respect to their time step parameter, which confirms that the frequency inaccuracies tend towards zero as the time step does.

Similarly, the energy inaccuracy for both time integration schemes grows as the time step parameter increases, meaning a smaller δt provides a more accurate simulation with respect to energy.

The ideal time-step parameter has been chosen by estimating the maximum time step which will provide a simulation result with a relative frequency error smaller than 0.5% = 0.005. For the velocity Verlet integration scheme, $\delta t_{max} = 0.1$, and for the symplectic Euler integration scheme, $\delta t_{max} = 0.16$.
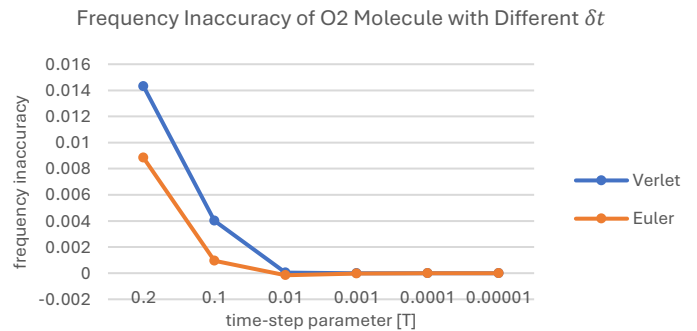
Simulation Results

Wave numbers (cm^{-1}) for molecules with particles that have initial velocities (0.05, 0, 0) and (-0.05, 0, 0):

	Velocity Verlet	Symplectic Euler
Oxygen	1531.7	1533.3
Nitrogen	2306.9	2327.8

Velocity Verlet: separation vs time of Oxygen particles

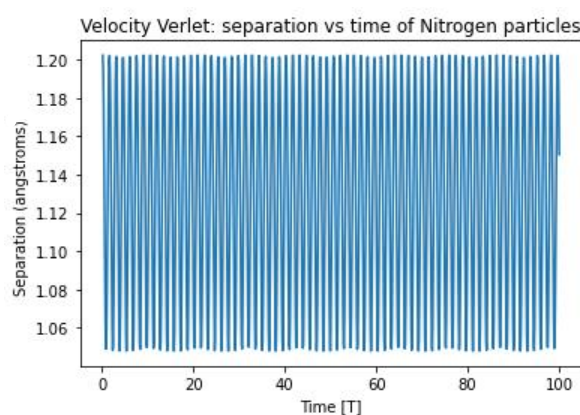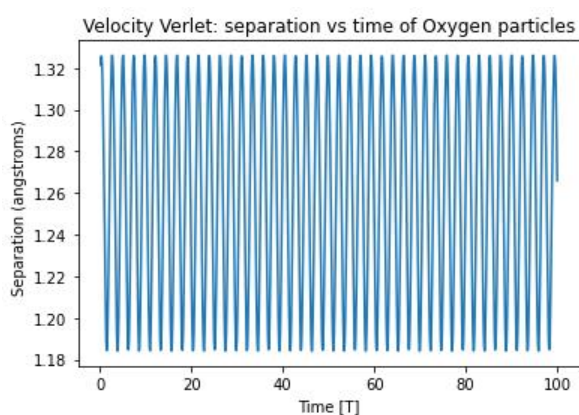Velocity Verlet: separation vs time of Nitrogen particles
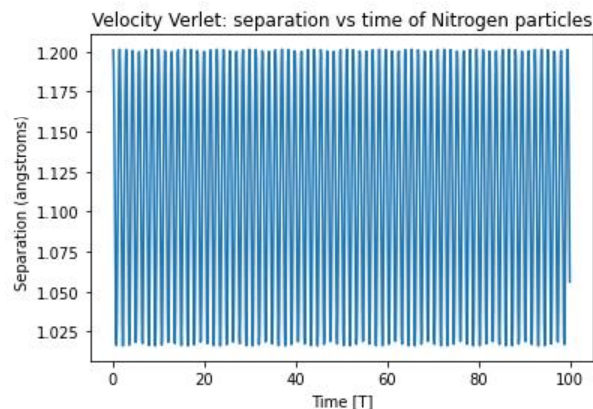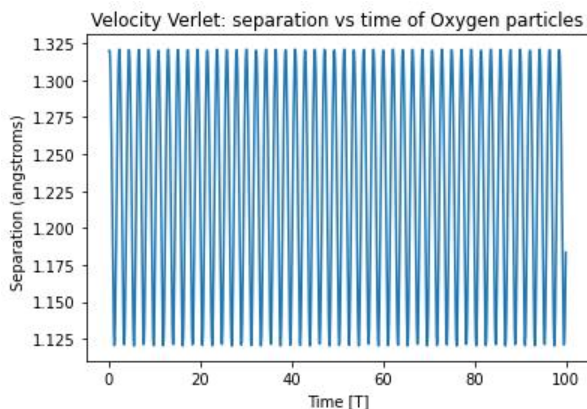
Wave numbers (cm^{-1}) for molecules with particles that have initial velocities (0.05, 0.3, 0) and (-0.05, -0.3, 0):

	Velocity Verlet	Symplectic Euler
Oxygen	1388.6	1382.8
Nitrogen	2204.4	2212.0

Velocity Verlet: separation vs time of Oxygen particles

Velocity Verlet: separation vs time of Nitrogen particles

Both integration schemes produce extremely similar results at the chosen time steps, hence only one has been shown.

Discussion

While a perfect simulation would conserve energy, these simulations will have a total energy that oscillates. The more inaccurate the simulation, the larger those oscillations and the larger the energy inaccuracy. In general, the energy inaccuracy for the velocity Verlet integration scheme was consistently and significantly lower than the energy inaccuracy for the symplectic Euler integration scheme, making it a seemingly more accurate simulation.

A comparison to the experimental values of the wave numbers (2359 cm^{-1} for nitrogen and 1580 cm^{-1} for oxygen) shows that the simulations were reliable. While the experimental values were not within 0.5% of the simulation values without spin, they are all roughly within 1-3% of them, which is quite successful. Interestingly, the symplectic Euler wave numbers without spin were closer to the experimental values than the velocity Verlet results without spin, suggesting the Euler integration scheme may provide more realistic results.

The purely vibrational frequencies (where the initial velocities are one-dimensional) result in higher wave numbers than the rotational frequencies (where the initial velocities are multi-dimensional). For the rotational frequencies, the particles are moving in both the x and y directions. As seen to the right, the particles move away from each other in the y direction as they move towards each other in the x direction, and vice versa. This means that their separation will take longer to oscillate, and thus the molecules will have a larger time period and smaller wave number than a purely vibrational frequency.

The Taylor expansion of the Morse potential energy to the second degree is: $U_M = D_e(\alpha^2 r_{12}{}^2 - 1) = D_e \alpha^2 r_{12}{}^2$, where we can ignore the "-1" since the zero of potential energy is arbitrary. Comparing this to the potential for simple harmonic motion, $U_{SHM} = \frac{1}{2}kx^2$, we can get a harmonic approximation for $\bar{v} = \frac{1}{2\pi c}\sqrt{\frac{2D_e\alpha^2}{m}}$ where $k = 2D_e\alpha^2$.

Velocity Verlet: x position vs time of Nitrogen spin particle

Velocity Verlet: y position vs time of Nitrogen spin particle