

# H1b 9: Molecular Dynamics

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Task N°	Points	Avail. points
$\Sigma$		

## Introduction

Simulating and analyzing a set of interacting aluminium particles using molecular dynamics. This is done using the Verlet algorithm as a numerical solution to Newton's equations of motion.

### Problem 1

By computing the potential energy in the aluminium lattice with a varying lattice constant we can approximate the lattice constant that corresponds to the lowest energy potential. In fig. 1 we can see the systems potential energy / unit cell against its volume. From the quadratic fit, implemented in Python, the lowest point is at  $65.416 \text{ \AA}^3$  or a lattice parameter of  $4.029 \text{ \AA}$ .

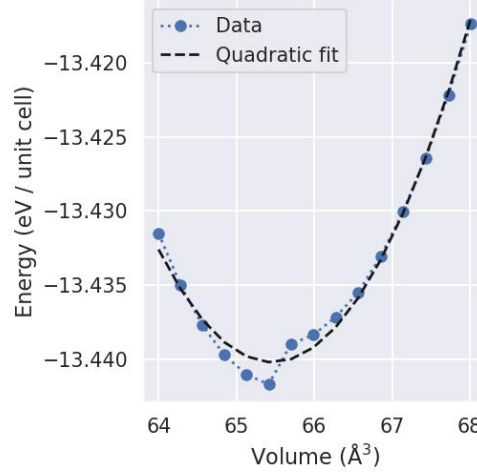


Figure 1: Energy - Volume graph of aluminium with quadratic fit along with the simulated values.

### Problem 2

The verlet algorithm was used here to solve the equations of motion and to simulate the particles trajectories, the algorithm is defined as the following,

$$\begin{aligned} \mathbf{v}(t + \Delta t/2) &= \mathbf{v}(t) + \frac{1}{2}\mathbf{a}(t)\Delta t, \\ \mathbf{r}(t + \Delta t) &= \mathbf{r}(t) + \mathbf{v}(t + \Delta t/2)\Delta t, \\ \text{calculate new accelerations: } &\mathbf{a}(t + \Delta t), \\ \mathbf{v}(t + \Delta t) &= \mathbf{v}(t + \Delta t/2) + \frac{1}{2}\mathbf{a}(t + \Delta t)\Delta t. \end{aligned}$$

Where this corresponds to one iteration / timestep and the first iteration starts with calculating the acceleration. In the verlet algorithm, an appropriate timestep has to be chosen to approximate the trajectories closely and not miss high frequencies but not too small to waste computation time. If the timestep is too large the total energy will drift and therefore not be conserved, as can be seen in fig. 2a, where it uses a timestep of  $\Delta t = 15 \text{ fs}$ . There is also the case where the  $\Delta t$  is slightly too large and the total energy drifts slowly, which can be seen in fig. 2b. Ultimately the energy is conserved when the timestep is just small enough with  $\Delta t \lesssim 5 \text{ fs}$ , an example of this is seen in fig. 2c which uses a timestep  $\Delta t = 5 \text{ fs}$ . When the total energy is conserved an approximation of its mean temperature can be made using

$$\langle T \rangle = \frac{2\langle K \rangle}{3Nk_B},$$

where  $K$  is kinetic energy and  $N$  is the number of atoms, results in  $\langle T \rangle \approx 454.5 \pm 1 \text{ C}^\circ$ .

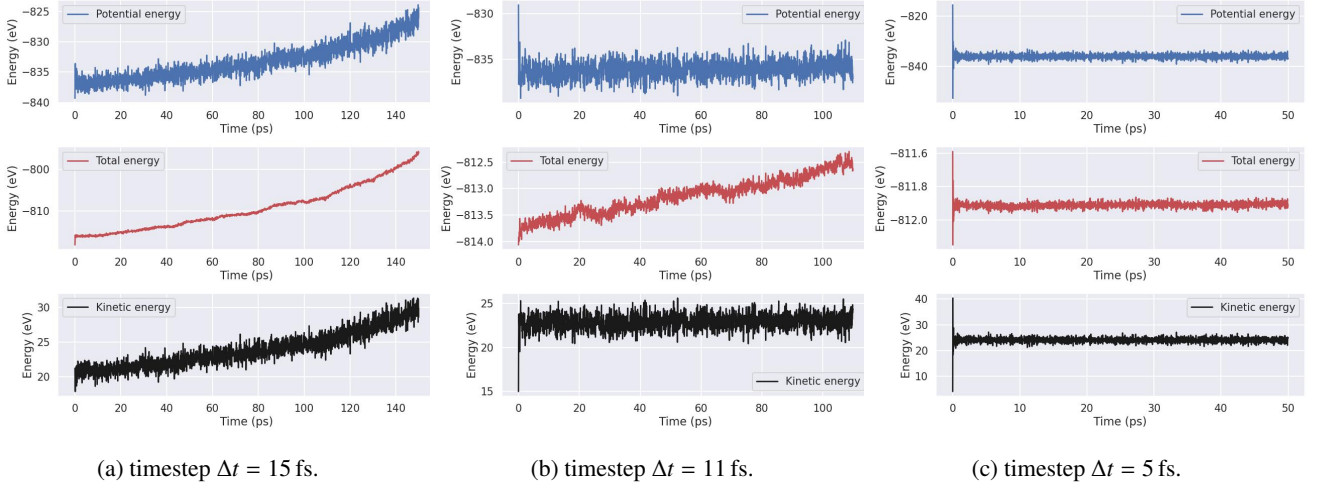


Figure 2: Kinetic, potential, and total energy for the system in using three different timesteps: one too large with  $\Delta t = 15$  fs, one a bit too large with  $\Delta t = 11$  fs, and one small enough with  $\Delta t = 5$  fs. A total of 10 000 steps are calculated.

## Problem 3

Implementation of equilibration routines. The isothermal compressibility constant that was used for both the solid and the liquid phase,  $\kappa_T = 2.584 \text{ \AA}^3 \text{ eV}^{-1}$ , based on the inverse of the bulk modulus[1].

To reach a certain temperature and pressure after the initial equilibration time, a scaling factor can be applied to the velocity  $\mathbf{v}_i^{\text{new}} = \alpha_T^{1/2} \mathbf{v}_i^{\text{old}}$ , and the particles positions and cell size  $\mathbf{r}_i^{\text{new}} = \alpha_P^{1/3} \mathbf{r}_i^{\text{old}}$ . Where the scaling factors are

$$\alpha_T(t) = 1 + \frac{2\Delta t}{\tau_T} \frac{T_{eq} - T(t)}{T(t)},$$

$$\alpha_P(t) = 1 - \kappa_T \frac{\Delta t}{\tau_P} (P_{eq} - P(t)).$$

The time constants  $\tau_T, \tau_P$  were finally set at  $\sim 200\Delta t$ , after trial and error. A total of 20 000 iterations were used with a timestep of  $\Delta t = 5$  fs and the system reaches equilibration after approximately 7.5 ps or 1 500 iterations, that is when  $\langle P \rangle$  approaches  $P_{eq}$ . In fig. 3a the time series during the equilibration run of pressure and temperature can be seen. The temperature of the system reached the intended  $\langle T \rangle = 500.2 \pm 2.8 \text{ }^\circ\text{C}$ , but the pressure of the system had larger deviations around  $P_{eq}$  and ultimately reached an average pressure of  $\langle P \rangle = 200 \pm 250$  bar. The lattice constant reached a value of  $\langle a_0 \rangle = 4.09016 \pm 0.00036 \text{ \AA}$ . To not influence the mean of the temperature and pressure with the  $\alpha$ -scaling during the simulation, the run is divided into three parts. The first one equilibrates the system  $N = 1\,500$  iterations, the second one approximates the mean for the lattice constant  $a_0$  with  $N = 8\,500$  iterations and the last one is with a constant  $a_0$  for calculating the mean, standard deviation for  $T, P$  with  $N = 10\,000$  iterations.

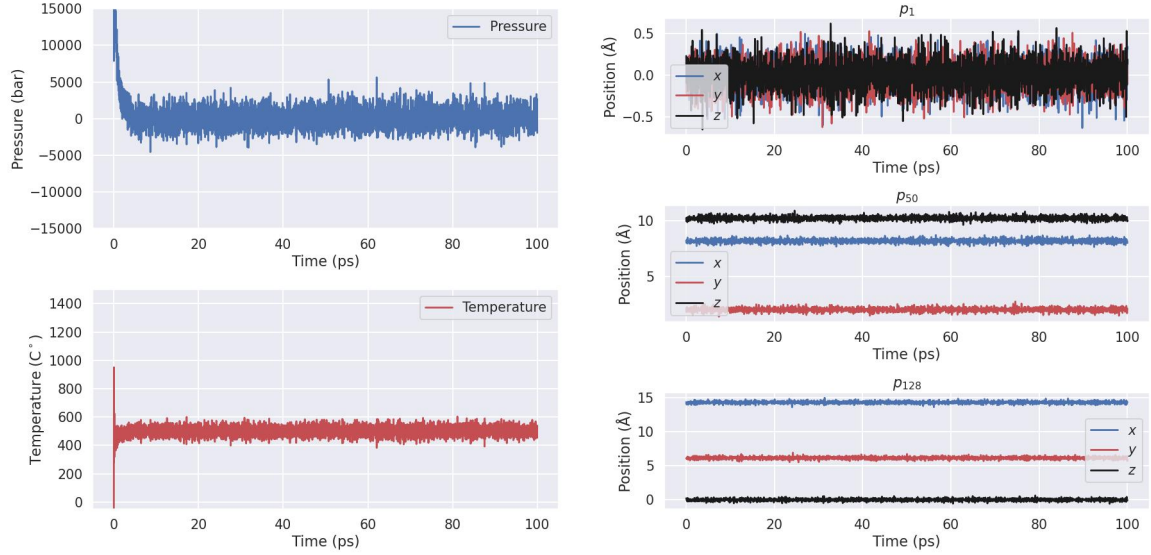
In fig. 3b, the positions of three particles in the system can be seen to verify state of the system. As can be seen the particles do not reach larger deviations from their initial positions later in the simulation and there by verifies that the system is in a solid state.

In all of the following graphs, the system in a solid state will be using  $T_{eq} = 500^\circ \text{C}$ ,  $P_{eq} = 1$  bar, with a initial deviation of 6.5% and the system in a liquid state will be using  $T_{eq} = 700^\circ \text{C}$ ,  $P_{eq} = 1$  bar, with an initial deviation of 35%.

## Problem 4

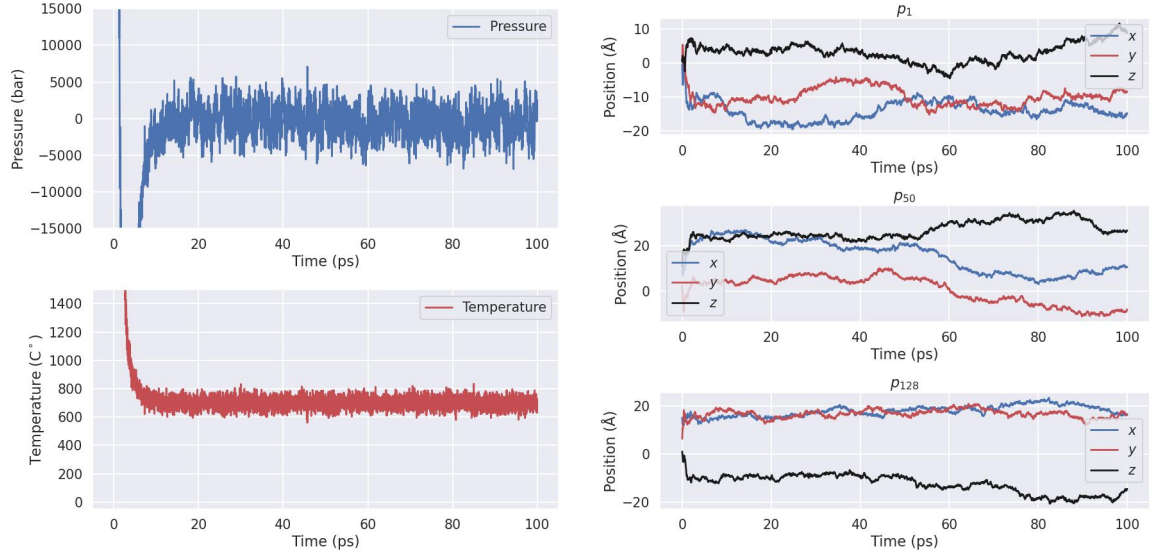
Equilibration to a higher temperature of  $T_{eq} = 700^\circ \text{C}$ ,  $P_{eq} = 1$  bar, and intended to reach a liquid state, using largely the same method as in the previous problem.

In order to have enough energy in the system to melt it, larger initial deviations of particle's positions were chosen, from  $\pm 6.5\%$  to  $\pm 35\%$  of the lattice parameter. The systems mean temperature reached  $\langle T \rangle = 700 \pm 3 \text{ }^\circ\text{C}$  and pressure of the system reached  $\langle P \rangle = -500 \pm 200$  bar, with a lattice constant of  $\langle a_0 \rangle = 4.255 \pm 0.006 \text{ \AA}$ . dict



(a) Instantaneous pressure and temperature of the solid system. (b) Trajectories of three particles from system in a solid state.

Figure 3: Equilibration of the solid state system.



(a) Instantaneous pressure and temperature of the liquid system. (b) Trajectories of three particles from system in a liquid state.

Figure 4: Equilibration of the liquid state system.

## Problem 5

What is the mean squared displacement (MSD) of the system in the two different states? The mean squared displacement was defined mathematically as

$$\Delta_{MSD}(t) = \frac{1}{N} \sum_{i=1}^N [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2.$$

For a solid the mean squared displacement goes towards a constant given enough time,

$$\lim_{t \rightarrow \infty} \Delta_{MSD}(t) = 6d_{th}^2,$$

where  $d_{th}$  is the mean thermal displacement of a particles position from its lattice position[2]. The thermal displacement for the solid system was measured to be  $d_{th} = 0.167 \pm 0.005 \text{ \AA}$ , and was calculated from the time average of the  $\Delta_{MSD}(t)$  when the system was equilibrated.

For a liquid  $\lim_{t \rightarrow \infty} \Delta_{MSD} \propto t$ , i.e MSD increases linearly with time after equilibration. The self-diffusion coefficient, from Fick's law of diffusion, is defined as  $D_s = \lim_{t \rightarrow \infty} \frac{\Delta_{MSD}(t)}{6t}$  and its value was approximated to  $D_s \approx 0.775 \text{ \AA}^2/\text{ps}$ , this appears

reasonable and matches experimental data. The  $D_s$  value was calculated from a linear fit of the  $\Delta_{MSD}(t)$ . In fig. 5a the MSD is shown for the system in the liquid state and in fig. 5b the system is in a solid state.

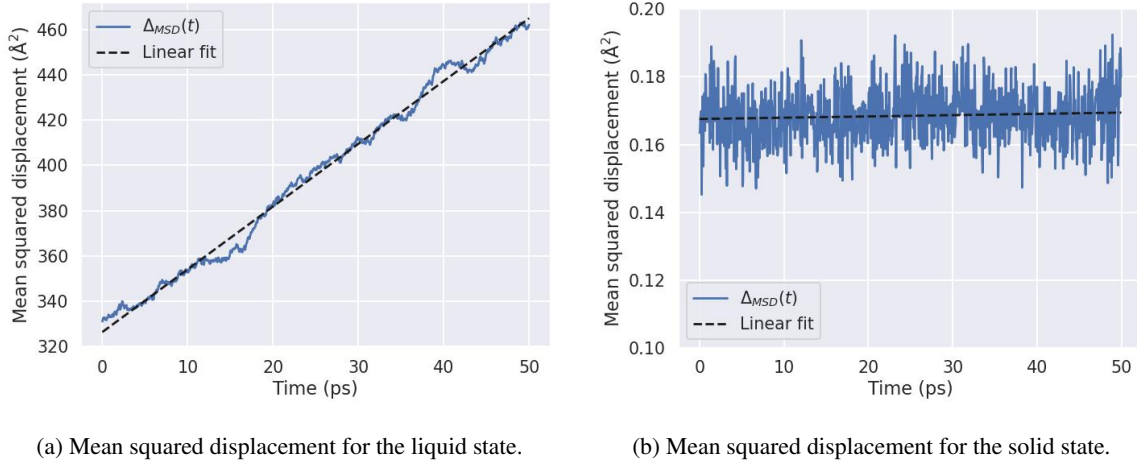


Figure 5: Mean squared displacement  $\Delta_{MSD}(t)$  for the liquid state in the left figure and for the solid state in the right figure.

## Problem 6

Velocity correlation function (VCF)  $\Phi(t)$ , is defined as

$$\Phi(t) = \frac{1}{N} \sum_{i=1}^N \langle \mathbf{v}_i(t + t') \cdot \mathbf{v}_i(t') \rangle = \frac{1}{N} \frac{1}{M-t} \sum_{i=1}^N \sum_{j=0}^{M-t-1} \mathbf{v}_i(t + j\Delta t) \cdot \mathbf{v}_i(j\Delta t),$$

where  $t = k\Delta t$ ,  $k = 0, 1, \dots, (M-1)$ .

In fig. 6 this definition of the VCF is used and gives a function that quickly reduces to zero. Another way of obtaining the VCF is through Fourier transforms, this is because VCF is a convolution of the velocity vectors.

$$\Phi(t) = \mathbf{v}(t) * \mathbf{v}(t) = \mathcal{F}^{-1} \left[ \mathcal{F} [\mathbf{v}(t)]^2 \right].$$

The VCF from the inverse Fourier transform can be seen in fig. 7a.

There is a resemblance between the two VCFs, with the main difference being the VCF from the IFFT being strictly positive while the other VCF quickly (0.5 ps) reaches negative values. Both VCFs have been normalized so that  $\Phi(t = 0) = 1$  and with units of  $\text{\AA}^2/\text{ps}^2$ . Note that fig. 7a uses logarithmic scaling for the y-axis.

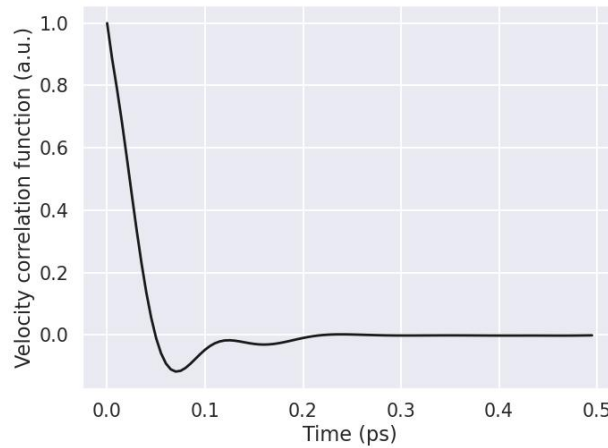


Figure 6: The velocity correlation function of the system in a liquid state, after normalizing  $\Phi(t = 0) = 1$ .

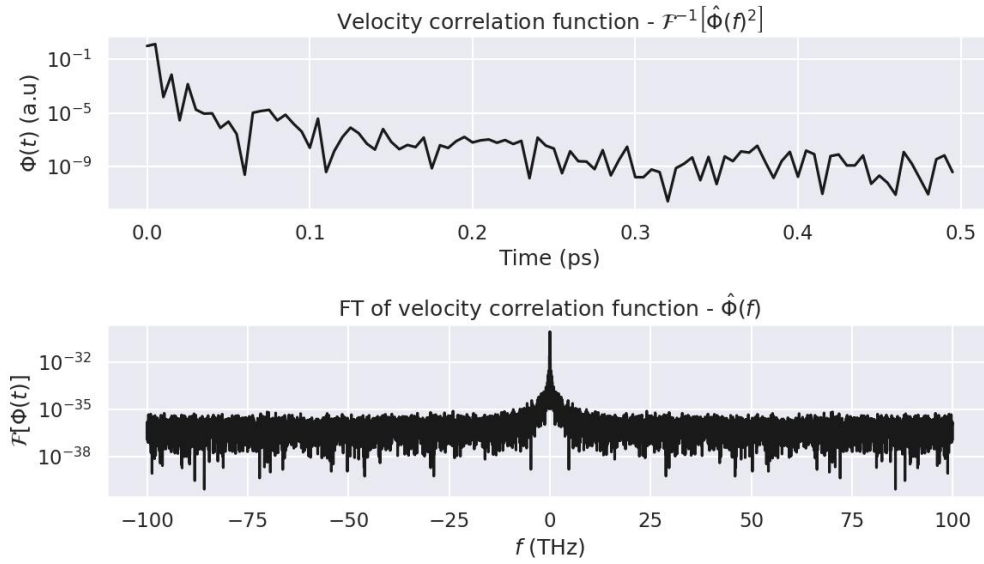


Figure 7: The velocity correlation function  $\Phi(t)$  obtained from the IFFT in the upper figure and the FFT of  $\Phi(t)$  in the lower figure.

## References

- [1] Engineering ToolBox, (2008). Metals and Alloys - Bulk Modulus Elasticity. [online] Available at: [https://www.engineeringtoolbox.com/bulk-modulus-metals-d\\_1351.html](https://www.engineeringtoolbox.com/bulk-modulus-metals-d_1351.html) [Accessed 20th November 2022].
- [2] Göran Wahnström, (2021). MOLECULAR DYNAMICS - Lecture notes.