

MD simulation - static properties

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Introduction

In this work we are going to investigate static properties of aluminum-particles in a molecular dynamics simulation. 256 particles are placed on a 3d grid with spacing a_0 in a box with periodic boundary conditions.

Problem 1

The first property we are going to investigate is how the potential energy of the system changes with volume (Figure 0.0.1). Interestingly the energy shows a minimum at a unit cell volume of about $V_0 = 65.45\text{\AA}^3$ when attractive and repulsive forces of the atoms cancel. This corresponds to the lattice constant a_0 for $T = 0K$, which then would be $(V_0)^{\frac{1}{3}} = 4.03\text{\AA}$. Measurements show that the real value is $a_0 = 4.0317\text{\AA}$ (2).

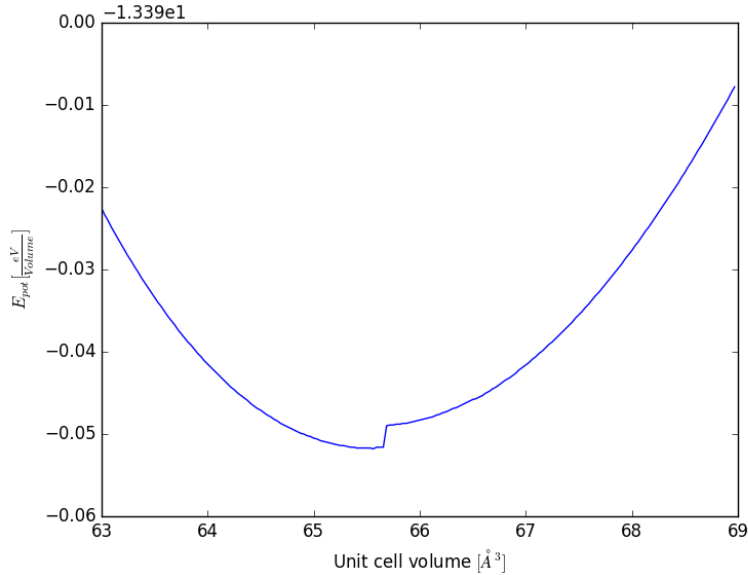


Figure 0.0.1: Potential energy of aluminum particles in a box in dependence of the unit cell volume.

Problem 2

We simulate the dynamics of the system using the velocity verlet algorithm, described in the lecture notes (1). An important parameter of the simulation is the lattice parameter $a_0 = 4.04\text{\AA}$. Particles are initialized with a random deviation of $\pm 0.065a_0$ around their position in a 3d grid. The resulting evolution of the energies can be seen in Figure 0.0.2. The chosen timestep is 0.005 ps (5 fs). From

the lecture notes we know, that a few femtoseconds are a typical size for an atomic system. The optimal timestep is a tradeoff between sampling through the phase space (large timestep) and accurate trajectories (small timestep)(1). We can observe from figure 0.0.2 that energy conservation is not given for a timestep of 0.05ps. Figure 0.0.3 shows for an even smaller timestep the evolution of energy. The results are quite similar to the 0.005ps timestep simulation. Moreover the continuous change of kinetic and potential energy can be seen (right graph). The energy is strictly conserved. When energy is conserved we can measure the average temperature to be approximately 806 K. The value is fluctuating a lot however and even averages over a long time will still have a considerable variance.

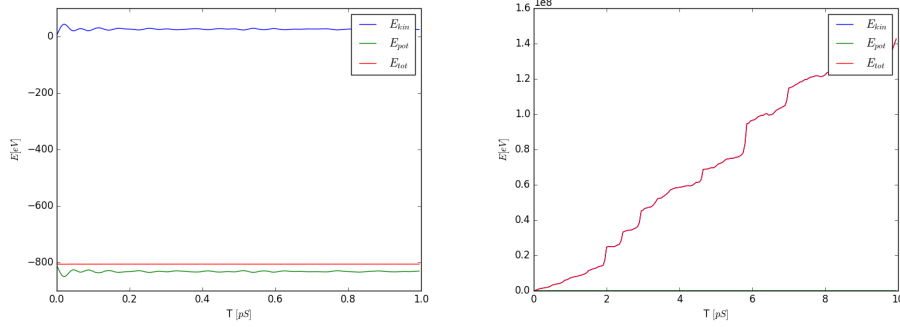


Figure 0.0.2: Evolution of the potential, kinetic and total energy over time. The left plot shows the results for a timestep of 0.005 ps, right for 0.05 ps. If the timestep is too long the algorithm is not able to integrate the motion properly anymore and the total energy of the system is not conserved. Tests showed that also bigger timesteps (e.g. 0.01 ps) are stable for short times. We will use the timestep of 0.005 ps for the rest of the simulations however, to keep a safety margin.

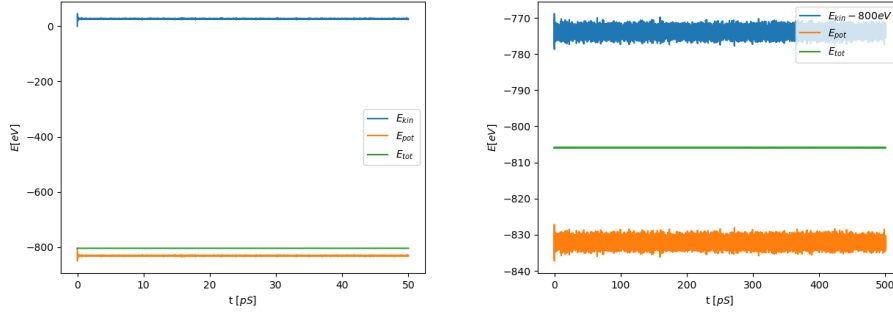


Figure 0.0.3: Evolution of the potential, kinetic and total energy over time. The left plot shows the result for a timestep of 0.5fs (0.0005ps). The energy is again conserved but there is not more information to extract than using a bigger timestep of 5fs. The right plot shows for the simulation using a 5fs (0.005ps) timestep the evolution of the energy over time. The potential energy is shifted by -800 eV.

Problem 3

As it is not possible to initialize the system with a desired temperature and pressure we now implement a routine to tune it towards them. This can be achieved by relating a change of the velocities for the temperature and of the lattice constant and positions (scaling of the system) for the pressure to the respective difference between an instantaneous and a desired value (for details see (1)). The relation can be chosen such that the difference decreases exponentially and essentially boils down to the form $y = f(x)$, $\tau \dot{x} = y_{ref} - y$ where y is the (normalized) temperature/pressure, x a variable it depends on through a (monotonous) function f and y_{ref} the desired value. Via τ the speed of the equilibration can be changed. As the pressure fluctuates more heavily than the temperature it proved advantageous

to use a bigger τ for it's evolution. For all of the simulations values for the timeconstants have been chose to be in the ranges $\tau_{temp} = 1 \dots 4ps$, $\tau_{press} = 2 \dots 8ps$. For the simulation we used $\tau_{temp} = 2ps$, $\tau_{press} = 3ps$.

The first goal is a system with a pressure of 1 bar and a temperature of 500 °C (Figure 0.0.4). Aluminum is a solid for these parameters which we can test by looking at the time evolution of the positions of the particles (Figure 0.0.5). After the calibration the volume of the system is approximately 4386 Å³ so the lattice parameter $a_0 \approx 4.092\text{\AA}$. The temperature and pressure reached the desired values, though, due to the violent fluctuations, with considerable inaccuracy (e.g. $T = 506^\circ C$, $P = 108bar$ averaged over 60 ps). In comparison to the variance of the fluctuations the deviations from the desired values for the equilibration are relatively small, also they do not get more accurate by using a longer equilibration time. Nevertheless, that the fluctuations itself are so big is not advantageous and could be changed by using a bigger system.

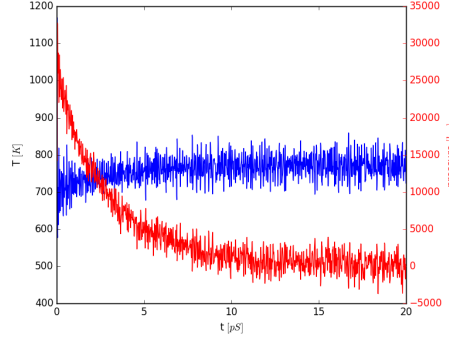


Figure 0.0.4: Evolution of temperature and pressure over time during the equilibration procedure. The pressure fluctuates in a regime of several hundred bars, so tuning it to 1 bar can result in negative pressures.

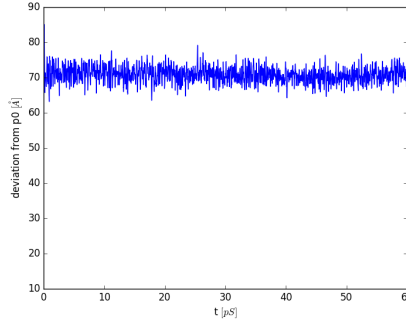


Figure 0.0.5: Evolution of the sum of the deviations of all particles from their starting point. The deviation stays (after an initial transient) constant over time. This indicates that the system is in a solid phase.

Problem 4

Now we tune the system to a temperature of 700 °C and a pressure of 1 bar (Figure 0.0.7). As we see, it experienced a phase transition and now is in a liquid state (Figure 0.0.8). After the calibration the volume of the system is approximately 4939 Å³ so the lattice parameter $a_0 \approx 4.258\text{\AA}$ ($T = 702^\circ C$, $P = -34bar$, the negative pressure comes from the fluctuations). Again, the results are - considering the size of the fluctuations - accurate enough. The equilibration procedure in this case takes a lot more time, as the interactions of pressure and temperature are larger due to the heating process.

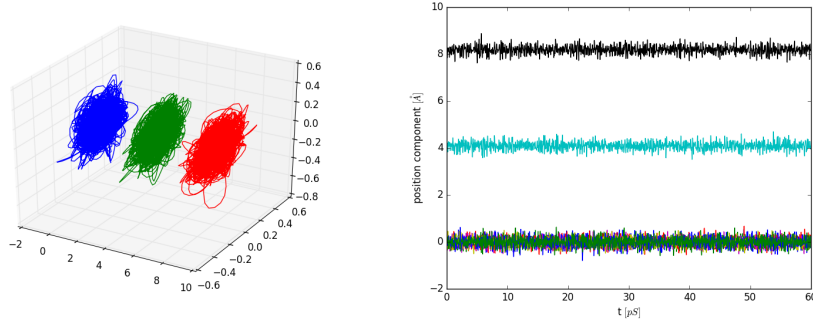


Figure 0.0.6: Evolution of the positions of three particles. The deviation stays (after an initial transient) constant over time and also the particles seem to oscillate around a fixed point in a 3d-grid. This indicates that the system is in a solid phase.

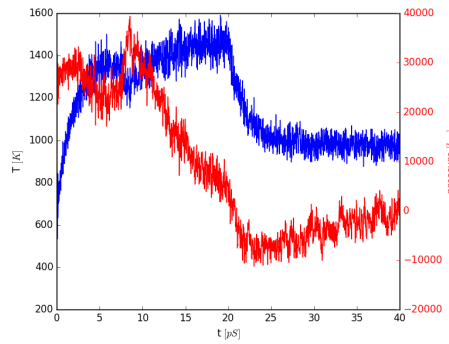


Figure 0.0.7: Evolution of temperature and pressure over time during the equilibration procedure. To efficiently bring the system into a liquid state we first 'heat' it up to 1200 °C and subsequently cool it down to 700 °C. The pressure is affected by the kinetic energy of the system as well, which is why it doesn't converge simply exponentially to the desired value.

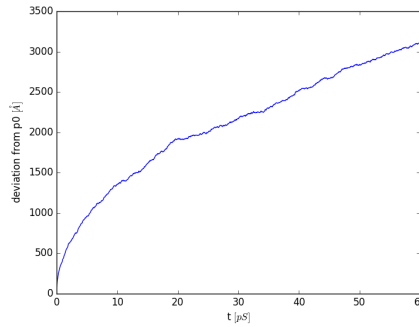


Figure 0.0.8: Evolution of the sum of the deviations of all particles from their starting point. The deviation now grows linearly over time (after a transient) where the slope is determined by a diffusion constant.

Problem 5

In this task we are finding the heat capacity of the system. This is an extensive property of the system related to the specific heat capacity, an intensive property of aluminum in this case. It can be found in the literature (3) to be $0.0904 \frac{\text{Å}^2}{\text{ps}^2 \text{K}}$ for the solid phase and $0.118 \frac{\text{Å}^2}{\text{ps}^2 \text{K}}$ as a liquid which means it takes more energy to heat up when in a liquid phase. The heat capacity then is the specific heat times the system mass $M = 256m_{Al} = 0.716 \frac{\text{eV ps}^2}{\text{Å}^2}$. We will instead look at the intensive variable $(\frac{C_V}{M})$ to compare it to the empirical values. By looking at the fluctuations of kinetic and potential energy

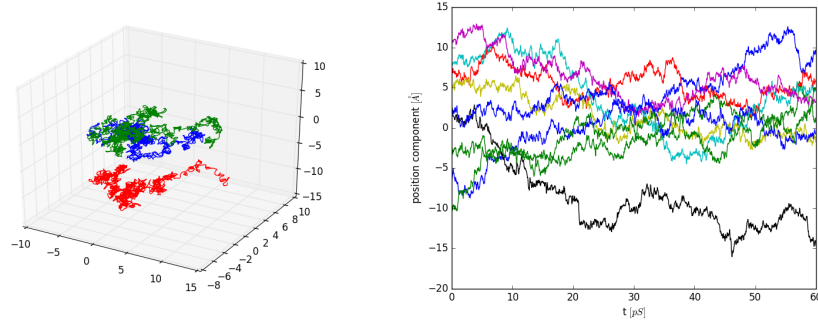


Figure 0.0.9: Evolution of the positions of three particles. Three dimensional representation (left). Two dimensional representation (right). Individual positions now follow a brownian motion.

while pressure and particle number are kept fixed we can estimate this value from the simulation with the formula given in the lecture notes.

It is interesting to see that even though the variance of potential and kinetic energy should be the same, we measure different values of C_V for both. So even if both energies approximately add up to the same value over the course of the simulation, their variance is ever so slightly different, also because the pressure of the (small sized) system is fluctuating, which we can't control. Another observation is that both estimates for 500°C and 700°C are between the empirical values. As the standard deviation of the estimates are rather small for 10 experiments it seems that the simulation doesn't quite capture all important characteristics of the systems, or the initialization is too inaccurate due to the small system size.

Table 0.0.1: Mean and standard deviation for C_V/M for 500°C (left) and 700°C (right) for 10 simulations each running for 60ps . All values have the units $\frac{\text{\AA}^2}{\text{ps}^2\text{K}}$.

	mean	std		mean	std
E_{pot}	0.0977	0.005	E_{pot}	0.0979	0.006
E_{kin}	0.0952	0.006	E_{kin}	0.0957	0.005

Problem 6

Another way to evaluate C_V is by using the equality $C_V = \frac{\partial E}{\partial T}$ and evaluating the differential with a finite difference method. In order to do that we first equilibrate the system to a certain temperature T and then keep the volume fixed while tuning it to two different temperatures $T \pm \Delta T = T \pm 1\text{K}$. We then measure the mean energies e_1 , e_2 and temperatures T_1 , T_2 of the system and can approximate C_V by $\frac{e_1 - e_2}{T_1 - T_2}$.

For our system we find at 500°C $C_V = 0.070 \frac{\text{eV}}{\text{K}}$, so $C_V/M = 0.097 \frac{\text{\AA}^2}{\text{ps}^2\text{K}}$. For 700°C $C_V = 0.085 \frac{\text{eV}}{\text{K}}$, so $C_V/M = 0.117 \frac{\text{\AA}^2}{\text{ps}^2\text{K}}$. While these values, given the empirical ones, seem to be more accurate than the values obtained in task 5, this method only really becomes useful for very long averaging times, which makes it difficult to tell the variance of the results.

Problem 7

Another static property of the system is how the positions of particles are correlated. This can be evaluated with the radial distribution function $g(r)$, which gives the probability of, given one atom, finding another atom at a distance r (Figure 0.0.10). First we equilibrate the system to 700°C , then we calculate the distances between the particles and sort them into bins to find $g(r)$. It is important to

keep in mind that we also have to check the neighboring 'images' of the system or else long distances will not be present and the function would go to zero for $r \rightarrow \infty$. Having this function we can find the coordination number of the system. First we find the first minimum of $g(r)$ which is at $r_m \approx 3.79$. Then we integrate $g(r)$ over the sphere up to that point to find the expected number of atoms within that distance. We find $I(r_m) \approx 11.6$, which means that there are about 12 neighboring atoms. This sounds reasonable as tightly packed spheres would have exactly 12 neighbors, while we observe less due to the liquid nature of the system (literature-values for liquid aluminum were hard to come by).

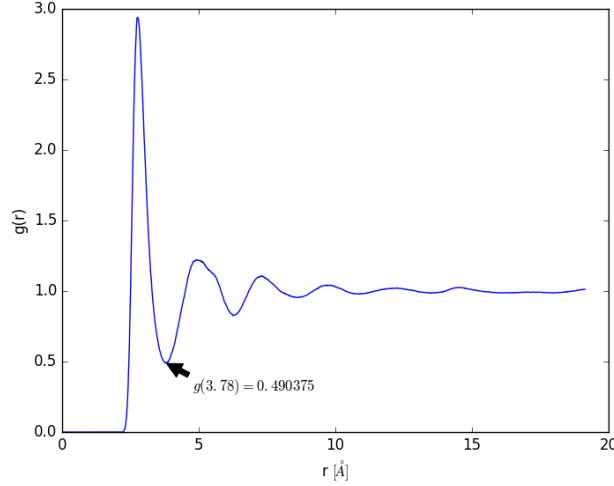


Figure 0.0.10: Radial distribution function $g(r)$.

Problem 8

The last property we will analyze is how incident radiation would be scattered by the liquid at 700 °C, which is quantified by the structure factor $S(q)$ (Figure 0.0.11). We evaluate it with the assumption that it's static.

The 3d-grid method works as following. The 3d grid is essentially a 3d fourier space where we add up contributions of all particles to the scattering, where each atom adds the term $\exp\{i\mathbf{q} \cdot \mathbf{r}\}$. In the end we average over the sphere in order to get a function $S(q)$ which only depends on the length of \mathbf{q} and normalize it over the particles. As the grid has to be discretized it is important to choose appropriate spacing to make the contributions of particles outside the periodic boundaries to add up nicely. The individual components of the grid thus ranged from $-32\frac{2\pi}{L}, -31\frac{2\pi}{L} \dots 32\frac{2\pi}{L}$, where L is the length of the box.

References

- [1] Göran Wahnström, *Molecular dynamics -lecture notes*, 2018.
- [2] A K Giri and G B Mitra *Extrapolated values of lattice constants of some cubic metals at absolute zero*, Journal of Physics D: Applied Physics; 18-7,L75, 1985.
- [3] Tipler, P.A. and Mosca, G. *Physics for Scientists and Engineers*, Physics for Scientists and Engineers: Standard, W. H. Freeman, 2007

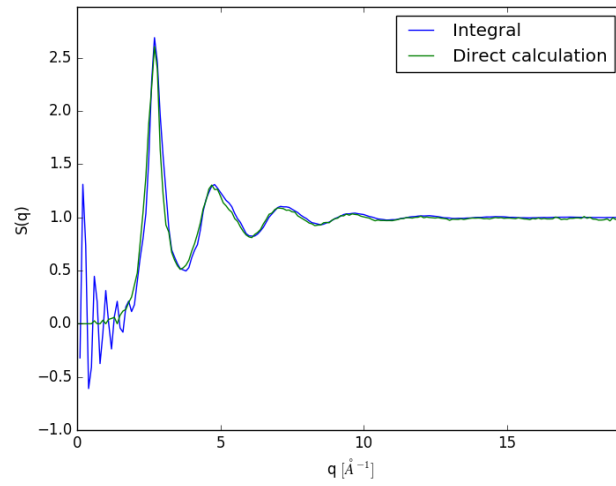


Figure 0.0.11: The static structure factor $S(q)$. Here we compare two different ways of calculating it: by fourier transforming the radial distribution function $g(r)$ and by direct calculation with a 3d-grid. The fourier-integral and the direct calculation give very similar results for a big part of the spectrum. For $q \rightarrow 0$ however, the integral calculation starts to oscillate excessively while the result for the direct calculation smoothly goes to zero. The reason is here that we cannot evaluate the integral numerically up to $r \rightarrow \infty$, so the oscillations of the fourier components do not cancel (yet).