

## H1a MD simulation - static properties

In this homework problem you are asked to use the molecular-dynamics (MD) simulation technique. You will study static properties of aluminum, both in the solid and liquid phase, using an appropriate inter-atomic potential. You should use the units introduced in appendix B in exercise E1, which are units suitable to use in atomic scale simulations. **Read the instructions for the report on the homepage.**

In the first part, task 1-4, you will develop a basic MD program in C. For your convenience a few C routines are provided. In the second part, task 5-8, you will analyze the output data and determine the heat capacity at constant volume  $C_V$ , radial distribution function  $g(r)$  and the static structure factor  $S(q)$ . Here you are asked to develop your own analysis programs.

### Task

1. Initiate a system of 256 Al particles on a fcc lattice. This should be done with the provided script `initfcc.c`. In order to construct a fcc lattice the syntax is

```
init_fcc(X, N, a0);
```

where `X` is a matrix (in which the atomic positions are stored), `N` is the number of unit cells in each direction and `a0` is the lattice constant. The potential energy (using periodic boundary conditions) of the system is computed with the provided script `alpotential.c`. The syntax is

```
E_pot = get_energy_AL(X, N * a0, natoms);
```

where `E_pot` is the variable in which the energy is stored. Compute the energy for a set of volumes and make sure that you can reproduce the data in Fig 1. What is the theoretical lattice parameter at 0 K? (1p)

2. Introduce small random deviations from the initial lattice positions. The displacements should be uniform in the interval  $\pm 6.5\%$  of the lattice spacing in each direction. Solve the equation of motion using the velocity Verlet algorithm, using periodic boundary conditions that are implemented in `alpotential.c`. Set the initial velocities to zero and study the time-evolution of the potential, kinetic and total energies. Compute the average temperature and check that it is around

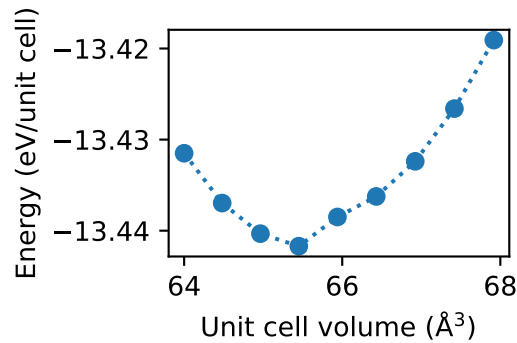


Figure 1: Energy-Volume diagram of aluminium.

600-800 K. What is a suitable time step? Vary the time step and investigate the effect on energy conservation. **Hint:** Read section 4.2 in the lecture notes "Molecular dynamics". (3p)

- Implement the equilibration routines described in appendix D in the lecture notes "Molecular dynamics". Note that the isothermal compressibility can be treated as a constant scaling of the time constant. Further, the isothermal compressibility is the inverse of the bulk modulus. You may use a tabulated value for the isothermal compressibility and the same value can be for both the solid and the liquid state. The time constants should be on the order of at least a few hundred time steps.

Equilibrate the system in the solid state, at  $T=500^\circ\text{C}$  and  $P=1$  bar. Notice that for the small system sizes used in the simulation study, the magnitude of the fluctuations is large. When equilibrating at low pressure the instantaneous pressure can become negative (see Fig. 2). What is the lattice parameter of the equilibrated system? **Hint:** It is useful to study the time-evolution of the simulation cell size for the pressure equilibration.

Determine the temperature  $T$  and pressure  $P$  using constant energy and volume simulation by making a time-average along the MD trajectory. Convince yourself that the system is in a solid state by plotting the components of the position as a function of time for a few different particles. Verify that the particles stay close to their initial positions also for long times. (4p)

- Repeat the previous task for the liquid state, at  $T=700^\circ\text{C}$  and  $P=1$  bar. Convince yourself that the system is in a liquid state by plotting the components of the position as a function of time for a few different particles. Verify that the particle trajectories deviate substantially from

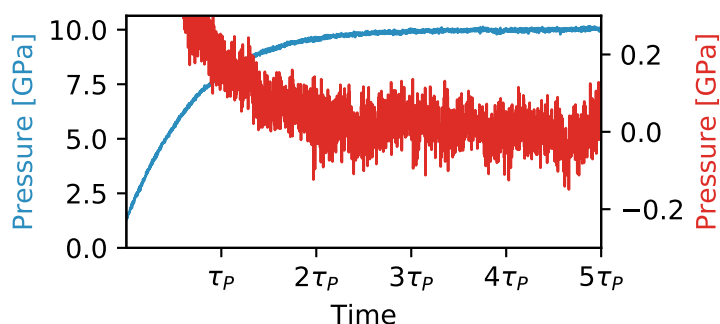


Figure 2: Example of fluctuations during pressure equilibration for high pressure equilibration (10 GPa) and low pressure equilibration (0 GPa).

their initial positions for long times. What is the lattice parameter of the equilibrated system? **Hint:** To melt the system it can be useful to first increase the temperature above  $T=700^\circ\text{C}$  and then decrease it to  $T=700^\circ\text{C}$ . (2p)

5. The fluctuations of the instantaneous kinetic and potential energies at constant  $NVE$  are related to the heat capacity at constant volume  $C_V$  for the system. Use the relations in section 7.1.2 in the lecture notes "Molecular dynamics" to determine  $C_V$  both for the solid state at  $T=500^\circ\text{C}$  and  $P=1$  bar and at the liquid state at  $T=700^\circ\text{C}$  and  $P=1$  bar. (1p)
6. Repeat the previous task but now use the relation

$$C_V = \left( \frac{\partial E}{\partial T} \right)_{N,V}$$

from thermodynamics. You should keep the volume  $V$  (and particle number  $N$ ) constant and change the temperature  $\pm\Delta T$  with some reasonable value for  $\Delta T$ . Then evaluate  $C_V$  using a finite difference approximation for the above derivative. Compare with the result in the previous task. (2p)

7. Consider now the liquid state system at  $T=700^\circ\text{C}$  and  $P=1$  bar. Determine the radial distribution function  $g(r)$  (see section 7.3.1 in the lecture notes "Molecular dynamics"). Evaluate also the coordination number  $I(r_m)$  by choosing  $r_m$  equal to the first minimum of  $g(r)$ . (3p)
8. Consider again the liquid state system at  $T=700^\circ\text{C}$  and  $P=1$  bar. Determine now the static structure factor  $S(q)$  by making a direct evaluation of Eq.(64) in the lecture notes "Molecular dynamics". You

have to introduce a three dimensional grid in  $\mathbf{q}$ -space. The  $\mathbf{q}$ -grid has to be consistent with the periodic boundary conditions, *i.e.*  $\mathbf{q} = (2\pi/L)(n_x, n_y, n_z)$  where  $n_x$ ,  $n_y$  and  $n_z$  are integers. Disregard the delta-function contribution at  $\mathbf{q} = 0$ . Perform a spherical averaging to obtain  $S(q)$ .

The static structure factor can also be obtained by integrating the radial distribution function according to Eq.(67) in the lecture notes "Molecular dynamics". Perform that integration and compare your results with the above direct evaluation of  $S(q)$ . (4p)