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# 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 a Neuroevolution potential (NEP) [1].

In the first part, task 1-4, you will develop a basic MD program in `C`. **Keep in mind that the runtime of your program will be rather long. Plan accordingly!** For your convenience a few `C` routines are provided. In the second part, task 5-7, 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.

**It is highly recommended to run your MD program and store the results for the trajectories.** You can then start to analyse your results based on the stored trajectories. You should use the "Atomic simulation units", introduced in appendix A in exercise E1.

Task 1-4 should be done in `C`. For some of the analyzes in task 5-7 you are allowed to use `Python`. However, the calculation of $S(q)$ is time-consuming so it is recommended to use `C` at least for that part.

You should present your results in a written report. **For instructions how to write the report, read the information on the homepage.**

## Task

1. The course Gitlab repo contains code that you may use as a starting point. In the `run.c` file provided to you (under `src/`), create a `n_atoms` by 3 matrix of coordinates representing atomic positions in an fcc lattice using the `init_fcc` function in `lattice.c`. The syntax for this is

   ```
   init_fcc(positions, N, lattice_param);
   ```

   where `positions` is the matrix in which the atomic positions are stored, `N` is the number of unit cells in each direction and `lattice_param` is the lattice constant. Use a $4 \times 4 \times 4$ supercell, i.e. so that the number of atoms `n_atoms` is 256. We encourage you to reuse your library from C4 for this and later tasks (put it in `tools.c` and `tools.h`). Run `make` to compile the program.

   Create fcc structures of different volume by varying the lattice constant and calculate the potential energy of each generated structure using the `get_energy_AL` function in `potential.c`, the syntax of which is

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

where `E_pot` is the variable in which the energy is stored. Write the lattice constant and the corresponding energies to file and determine the equilibrium lattice constant by doing a quadratic fit in `Python`. Make sure that you can reproduce the data in Fig. 1. What is the theoretical lattice parameter at 0 K? (1p)

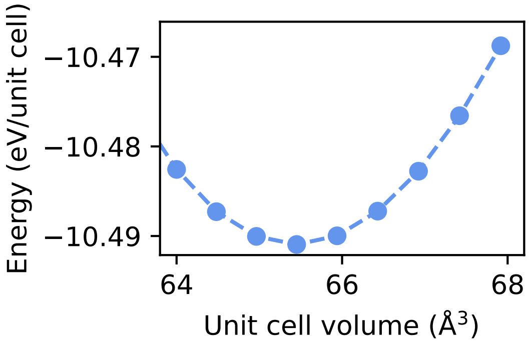

Figure 1: Energy-Volume diagram of aluminium.

2. Introduce small random deviations from the initial lattice positions. The displacements should be uniform in the interval ±6.5% of the lattice spacing in each direction. Solve the equation of motion using the velocity Verlet algorithm with periodic boundary conditions. Compute forces (and in later tasks virials) by calling `get_forces_AL` and `get_virial_AL` in `potential.c`. Alternatively, you can call `calculate`, which gives you all quantities at once, saving precious simulation time. You should not fold the atomic positions back into the simulation box, as the potential provided in `potential.c` correctly applies the boundary conditions.

   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 600-850 K. What is a suitable time step? Vary the time step and investigate the effect on energy conservation. How does the system behave with timesteps that are far too large, just a bit too large, and small enough? (You are, of course, expected to explicitly show this with plots and discuss them.) **Hint:** Read section 4.3 in the lecture notes "Molecular dynamics". The effects of a timestep that is barely too large can be very subtle. Carefully consider your plot limits! (3p)

3. Implement the equilibration routines described in appendix E 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 °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? Is it what you expect? **Hint:** It is useful to study the time-evolution of the simulation cell size for the pressure equilibration. **It is also a good idea to dump the simulation data to file, so that you can develop your analysis scripts separately from your simulation code.**

   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)

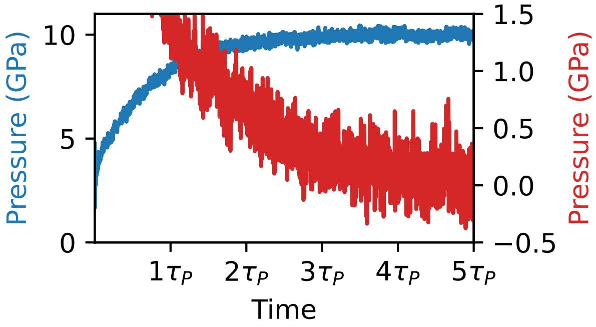

Figure 2: Example of fluctuations during pressure equilibration for high pressure equilibration (10 GPa) and low pressure equilibration (0.1 MPa).

4. Repeat the previous task for the liquid state, at $T$=700 °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

their initial positions for long times. What is the lattice parameter of the equilibrated system? Is it in line with what you would expect in comparison to that in Task 3? **Hint:** To melt the system it can be useful to first increase the temperature above T=700 °C and then decrease it to T=700 °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 °C and $P$=1 bar and at the liquid state at $T$=700 °C and $P$=1 bar. (2p)

6. Consider now the liquid state system at $T$=700 °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 $g(r)$. (4p)

7. Consider again the liquid state system at $T$=700 °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". Notice Eq. (68) that reduces the computational time by a factor $N$. You have to introduce a three dimensional grid in $\boldsymbol{q}$-space. The $\boldsymbol{q}$-grid has to be consistent with the periodic boundary conditions, *i.e.* $\boldsymbol{q} = (2\pi/L)(n_x, n_y, n_z)$ where $n_x$, $n_y$ and $n_z$ are integers. Disregard the delta-function contribution at $\boldsymbol{q} = 0$. Plot the static structure factor as function of $q$, the absolute value of the wave-vector $\boldsymbol{q}$. The calculation of the static structure factor will take some time on your computer. (4p)

# References

1. Fan, Z. *et al.* GPUMD: A package for constructing accurate machine-learned potentials and performing highly efficient atomistic simulations. *The Journal of Chemical Physics* **157,** 114801. `https://doi.org/10.1063/5.0106617` (2022).