

# Final projects

## Computational Physics course 2025

### Part 2: Molecular Dynamics

deadline 28<sup>th</sup> March, 2025

# 1) Molecular Dynamics – structure model

In this project you will implement molecular dynamics calculations for a gadolinium crystal, described using Lennard-Jones potential.

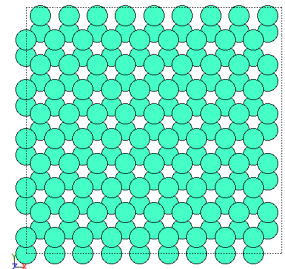
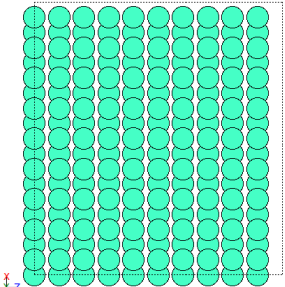
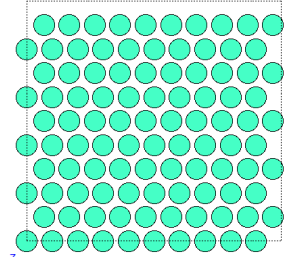
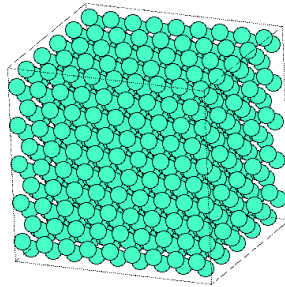
Gd crystallizes in a hexagonal close-packed crystal structure. Hexagonal unit cell is a bit inconvenient, since it doesn't have 90 degree angles between all of its axes, but it is possible to construct a bit larger unit cell, which has all angles equal to 90 degrees. Therefore, consider as the unit cell of gadolinium the following:

- Box dimensions are  $a \times \sqrt{3}a \times \sqrt{\frac{8}{3}}a$  where we will refer to  $a$  as the “lattice parameter”

- This unit cell contains four Gd atoms, which sit at fractional coordinates

$$\left(\frac{1}{4}, \frac{5}{6}, \frac{1}{4}\right), \left(\frac{1}{4}, \frac{1}{6}, \frac{3}{4}\right), \left(\frac{3}{4}, \frac{1}{3}, \frac{1}{4}\right), \left(\frac{3}{4}, \frac{2}{3}, \frac{3}{4}\right)$$

- A *super-cell*, that consists of  $9 \times 5 \times 5$  such orthogonal unit cells would contain 900 atoms and it would have lateral dimensions of a bit below 3nm in all three dimensions (assuming you set  $a=\sigma$ , see the definition of inter-atomic potential below) → see the pictures on the right side
- Consider [periodic boundary conditions](#) in all three dimensions



# 1) Molecular dynamics

Inter-atomic potential will be modelled purely by the empirical Lennard-Jones pair potential, given as in the lecture about molecular dynamics, i.e.,

$$V(\mathbf{q}) = \sum_{i \neq j}^N 4\epsilon \left[ \left( \frac{\sigma}{|\mathbf{x}_i - \mathbf{x}_j|} \right)^{12} - \left( \frac{\sigma}{|\mathbf{x}_i - \mathbf{x}_j|} \right)^6 \right]$$

where  $\sigma=3.304\text{\AA}$ ,  $\epsilon=0.1136\text{eV}$  and  $N=900$ . Be careful not to count any term twice – the sum goes over pairs of different atoms  $i,j$ . Use a cut-off of  $10\text{\AA}$ , beyond which the pair interactions will be neglected.

Although optional, but it is convenient to choose unit system, in which you won't need to use values with too high or too low orders of magnitude. You can get some aid from various unit systems used by LAMMPS (a widely used MD simulation software), see <https://docs.lammps.org/units.html>, e.g., the “real” or “metal” units can be quite convenient.

Hints: temperature, potential energy and kinetic energy can be calculated by

$$T = \frac{E_{\text{kin}}}{\frac{3}{2}Nk_B} \quad \text{where} \quad E_{\text{kin}} = \sum_{i=1}^N \frac{1}{2} m_i \mathbf{v}_i^2 \quad \text{and, clearly} \quad E_{\text{pot}} \equiv V(\mathbf{q})$$

# 1) MD: task 1a – auto-correlation function (10pts)

Implement Langevin dynamics (see the lecture slides about molecular dynamics) using the extended 5-step velocity Verlet algorithm. Use Box-Muller algorithm to generate normally distributed random numbers.

A position-position auto-correlation function for can be calculated in the following way

$$C(t) = \frac{\Delta t}{T - t} \sum_{\substack{t' \\ 0 < t' < T - t}} \frac{1}{N} \sum_{i=1}^N \frac{\langle \mathbf{r}_i(t') \cdot \mathbf{r}_i(t' + t) \rangle - \langle \mathbf{r}_i(t) \rangle \cdot \langle \mathbf{r}_i(t) \rangle}{\langle \mathbf{r}_i(t) \cdot \mathbf{r}_i(t) \rangle - \langle \mathbf{r}_i(t) \rangle \cdot \langle \mathbf{r}_i(t) \rangle}$$

where one averages over all atoms (the sum over  $i$ ) and over all time steps  $t'$ , such that  $t' + t < T$ , where  $T$  in this equation is the total length of the trajectory (careful: this should not be confused with temperature). Assume room temperature 300K in MD simulations and don't forget about the thermalization phase. Time  $t=0$  starts after the thermalization.

Calculate and plot the position-position auto-correlation function as a function of time delay  $t$ . Perform this calculation for a few different values of damping constant  $\gamma$ , e.g.,  $0.001 \text{ fs}^{-1}$ ,  $0.01 \text{ fs}^{-1}$  and  $0.1 \text{ fs}^{-1}$ . The maximum time delay  $t$  doesn't need to be taken too large, correlations usually drop relatively fast (~hundreds or few thousands of steps). Time step can be set to  $1 \text{ fs}$ .

An integral of this auto-correlation function is a so-called *correlation time*  $\tau$ . Calculate the correlation time  $\tau$  using Simpson's or Boole's method for each of the considered values of  $\gamma$ .

# 1) MD: task 1b – mean-squared displacement (15pts)

Knowing the correlation time  $\tau$  for  $\gamma=0.01 \text{ fs}^{-1}$  gives us the information, how often it is optimal to sample the atomic positions.

Sample now the atomic displacements  $\Delta \mathbf{r}_i(t) = \mathbf{r}_i(t) - \mathbf{r}_{i,\text{eq}}$  and evaluate so called *mean squared displacement*, which is an experimentally measurable quantity often determined by x-ray scattering experiments when measuring the crystal structures:

$$MSD = \frac{1}{N} \sum_{i=1}^N \frac{1}{N_\tau} \sum_{k=0}^{N_{\text{timesteps}}} \Delta \mathbf{r}_i(t_k) \cdot \Delta \mathbf{r}_i(t_k)$$

Do it as a function of temperature between ca 50K and 1000K at  $a=\sigma$  and plot it as a function of temperature. What trend do you observe?

Hint: You can sample either from every time point, or you can take an advantage of the known correlation time and take a measurement only every  $\sim \tau/(\text{time-step})$  steps. Note though that the correlation time may change with temperature.

# 1) MD: task 2 – equilibrium lattice parameter (25pts)

Calculate the total energy (sum of kinetic and potential energy) as a function of the lattice parameter  $a$ .

Extract the kinetic and potential energies from the trajectory by averaging them within the production phase (i.e., after the thermalization was completed). Vary the lattice parameter  $a$  between approximately  $0.8\sigma$  and  $1.2\sigma$  with a step of  $0.05\sigma$ .

The minimum of the total energy corresponds to the equilibrium lattice parameter. Fit the energy vs lattice parameter curve by a parabola and from the fit extract the equilibrium lattice parameter.

Perform the calculation at room temperature 300K as well as at a much lower temperature of 50K and at a much higher temperature of 1000K (and eventually at few additional temperatures within this range). What phenomenon do you observe?

# Hints and parameters

- \* Use a time-step of 1fs.
- \* Lennard-Jones potential parameters are  $\sigma=3.304\text{\AA}$ ,  $\epsilon=0.1136\text{eV}$ ,  $N=900$  and a cut-off of  $10\text{\AA}$ .
- \* Thermalization phase may take about 1ps, i.e., about 1000 time steps (verify!).
- \* Auto-correlation function is dimensionless, but the correlation time has units of seconds.
- \* Since atoms in a crystal typically don't move far from their equilibrium positions (square root of MSD can roughly tell you how far), it is a good idea to build a list of neighboring atoms for every atom in the structure model before starting the MD simulation. Such list would contain all atoms whose distance from the reference atom is lower than the cut-off radius of the potential (+ a bit of reserve, e.g., try  $12\text{\AA}$ ). Having and using such lists can offer a significant speed-up of the MD calculation. Pay attention in considering the periodic boundary conditions, when building these lists! As a cross-check: due to periodicity all atoms should have the same number of neighbors.