

## Assignment 4: Empirical potential construction and analysis

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In this assignment you will construct an embedded atom method (EAM) potential for aluminum. Using this potential you will then analyze different properties including the elastic constants, defect formation and migration energies, and the solid-liquid phase equilibrium.

“With four parameters I can fit an elephant, and with five I can make him wiggle his trunk.”

— John von Neumann

### Potential construction

#### 1 Background

Pair potentials, i.e., potentials with the functional form

$$E = \sum_i \sum_{j, j \neq i} V(r_{ij}) \quad \text{with} \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \quad (1)$$

are simple and computationally inexpensive but have various shortcomings. For instance, atomic bonds always have the same strength regardless of the environment. Also, the so called Cauchy relation  $c_{12} = c_{44}$  always holds [1]. This relation is violated by most materials, including the face-centered cubic (FCC) groundstate phase of aluminum, which we will consider in this task.

In the early 1980s several different groups of researchers arrived at conceptionally very similar forms that remedy the shortcomings for pair potentials for the case of metallic bonding [2–6]. These models are so-called pair functionals, the most prominent representative being the embedded atom method (EAM) [2]. In this formalism, the total energy is written as

$$E = \frac{1}{2} \sum_i \sum_{j, j \neq i} V(r_{ij}) + \sum_i F(\bar{\rho}_i) \quad \text{with} \quad \bar{\rho}_i = \sum_{j, j \neq i} \rho(r_{ij}), \quad (2)$$

where  $V$  is a pair potential,  $F$  is the so-called embedding function, and  $\rho$  is the electron density. The embedding term  $F(\bar{\rho}_i)$  accounts for the environmental dependence; it represents the energy associated with placing (“embedding”) the atom  $i$  in the electron density arising from the other atoms. The functions  $V$ ,  $F$  and  $\rho$ , which define the EAM potential, can be quite general and be chosen to depend on a large number of parameters. In terms of computational cost, the EAM potential is only about twice as expensive as a pair potential.

In ASE the easiest way to use EAM potentials is via the EAM calculator,<sup>1</sup> which supports reading and writing alloy format potentials. Mind though that molecular dynamics (MD) calculations within ASE based on this calculator are computationally inefficient.<sup>2</sup> The computational efficiency is, however, sufficient for fitting EAM potentials. For heavier computations, one can write out an alloy format potential file and use for example the popular MD code LAMMPS,<sup>3</sup> which is what you will be doing in the second part of the assignment.

<sup>1</sup> <https://wiki.fysik.dtu.dk/ase/ase/calculators/eam.html>

<sup>2</sup> This is because python is a scripting language, which (most of the time) is interpreted rather than compiled (and optimized).

<sup>3</sup> <http://lammps.sandia.gov/>

## 2 Our chosen parametrization

For our EAM potential, we choose the Finnis-Sinclair form  $F \propto \sqrt{\rho}$  [3] and the parametrization

$$V(r) = A \exp(-\lambda r) \quad (3)$$

$$F = D\sqrt{\rho} \quad (4)$$

$$\rho = \exp(2\mu r) \quad (5)$$

so that the potential is defined by only four parameters  $A$ ,  $\lambda$ ,  $D$ , and  $2\mu$ . In other words, the pair potential is a purely repulsive exponential and the bonding solely arises from the embedding term. The electron density is assumed to be exponentially decaying with distance. In order to have a finite interaction range and still get continuous energies and forces, we need to introduce a smooth cutoff function

$$f_c(x) = \begin{cases} x^4 / (1 + x^4) & x \leq 0 \\ 0 & x > 0 \end{cases} \quad (6)$$

and multiply  $V(r)$  and  $\rho(r)$  with  $f_c((r - r_{\text{cutoff}})/3)$  where  $r_{\text{cutoff}} = 6.5 \text{ \AA}$  in order for these functions as well as their derivatives to smoothly decay to zero and vanish at  $r_{\text{cutoff}}$ .

## 3 Fitting procedure

With a potential depending on a vector of parameters  $\alpha$  we can calculate a number of quantities  $A_i(\alpha)$ . To fit the potential one then minimizes

$$\chi^2 = \sum_i w_i \left( A_i^{\text{ref}} - A_i(\alpha) \right)^2, \quad (7)$$

where  $A_i^{\text{ref}}$  are reference quantities obtained from e.g., DFT or experiment and  $w_i$  are weights that control the relative importance of the different quantities as decided by the person constructing the potential.

## 4 Tasks

1. Begin by setting up your fit database. Download the reference configurations with forces from the ping-pong page. They are provided in ASE trajectory format and can be read using the `ase.io.read()` function. These configurations represent snapshots from an MD run at 900 K for an 108 atom FCC cell at 90%, 100%, and 110% of the equilibrium lattice parameter, where the forces were evaluated using the PBE exchange-correlation functional [7].
2. Use the suggested parametrization and fit your own EAM potential for aluminum using the forces that are provided with the reference configurations. A Python script containing a function that returns an appropriate ASE calculator can be downloaded from the pingpong page. Fit the parameters to the force components. You should also include the lattice parameter and cohesive energy in the fit. The 0 K lattice parameter for FCC Al is  $4.032 \text{ \AA}$  and the cohesive energy is  $-3.36 \text{ eV/atom}$ . You may use the starting guess  $(A, \lambda, D, 2\mu) = (1000 \text{ eV}, 3 \text{ \AA}^{-1}, 5 \text{ \AA}, 1 \text{ \AA}^{-1})$ . Also, the SciPy function `scipy.optimize.leastsq()` may be useful.  
Put  $w_i = 1$  for the force components and try to determine reasonable weights  $w_i$  for the cohesive energy and lattice parameter. What 0 K lattice parameter and cohesive energy do you obtain?  
What is the root mean square (RMS) deviation between the forces in your fit database and the ones predicted by your potential? To visualize the predictions by your potential plot the force components from the EAM potential against the DFT data.
3. Finally, plot your pair potential  $V$ , embedding function  $F$  and electron density  $\rho$ .

## Elastic properties and high-energy phases

### 1 Background

In order to characterize your potential, you will now calculate the elastic constants as well as the energy-volume curves of several hypothetical crystalline phases. The latter exercise serves as a demonstration for the ability (or inability) of your potential to predict properties (far) outside the range of properties considered during fitting.

## 2 Tasks

1. Use the method described by Mehl *et al.* [8] to calculate the elastic constants  $c_{11}$ ,  $c_{12}$  and  $c_{44}$ . Use the equations (11–14) from that reference to obtain  $c_{11}c_{12}$  and  $c_{44}$ . Then use “Strain 1” in Table 2 to get  $c_{11} + c_{22}$ . (In other words, do not obtain the bulk modulus from a fit to an equation of state here!) Which bulk modulus  $B = (c_{11} + 2c_{12})/3$  and tetragonal shear elastic constant  $c' = (c_{11}c_{12})/2$  do you obtain? Compare your results with experimental values and comment on them.
2. Compute the phonon dispersion relation and the density of states at the equilibrium lattice parameter. To this end, we recommend that you use the `ase.phonons.phonons` class. Compare your result with experiment and/or first-principles calculations available in the literature. Comment on your results. Then extract the sound velocity of the longitudinal acoustic mode along [100] in the limit  $q \rightarrow 0$  (the long-wavelength limit). The longitudinal sound velocity is related to the effective Young’s modulus  $Y$  in the respective direction according to  $c_s = \sqrt{Y/\rho}$ , where  $\rho$  is the mass density. Along [100] the respective Young’s modulus equals the elastic constant  $c_{11}$ . How does  $c_{11}$  from the sound velocity compare to the value you obtained above?
3. Calculate the energy as a function of volume (in the range between 80 and 120% of the equilibrium volume) for FCC Al as well as Al in the simple cubic, body-centered cubic, and diamond structures. Compare your results to the DFT data that you can find on the pingpong page. Fit the Birch equation of state, equation (1) in Ref. [8], to your  $EV$  curve for FCC Al. Calculate the bulk modulus using equation (2) in the same reference. Make sure the result is converged with respect to  $N$  (the order of the Birch fit). Does your result agree with the result obtained above?

## Solid-liquid phase equilibrium

### 1 Background

You will now examine both the solid and liquid phase at finite temperatures using molecular dynamics (MD) simulations as implemented in LAMMPS.

In particular, you will determine the melting point by simulating a solid-liquid interface. After preparation of the initial configuration, you will equilibrate several different copies of the system in the  $NPH$  ensemble (the so-called isenthalpic ensemble). The different simulations will differ by the amount of kinetic energy (i.e., the initial temperature).

If the average kinetic energy and thus the average temperature in the system is noticeably larger (smaller) than the actual melting temperature the system will melt (solidify). If the average kinetic energy is, however, sufficiently close to the melting temperature the system will establish an equilibrium between solid and liquid and the average temperature will equal the melting point. The procedure has been demonstrated in the lectures and you can find an example in the lecture slides.

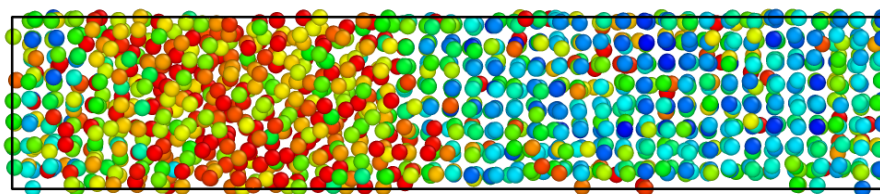


Figure 1: A snapshot from a co-existence melting point simulation.

### 2 Tasks

1. Use LAMMPS to compute the lattice thermal expansion up to 900 K. Compare with experimental results from literature.
2. Use the co-existence method with the  $NPH$  ensemble to determine the melting point with a *proper error estimate* for your Al potential.

An example LAMMPS script that you may find useful is provided on pingpong.

You should visualize the dump files of the atomic coordinates in order to ensure that solid and liquid are indeed in equilibrium. To this end it is strongly advisable to use the very powerful visualization and analysis software OVITO.

3. Determine the entropy of fusion, i.e. the increase in entropy upon melting. Use MD simulations in the  $NPT$  ensemble for two bulk systems at the melting point. Also determine the volume change upon melting. Find experimental values and compare.
4. Using the configurations obtained in the previous step, calculate the coordination numbers for the solid and the melt. The (first) coordination number  $n_1$  is defined through the radial distribution function  $g(r)$  as

$$n_1 = 4\pi \int_0^{r_1} r^2 g(r) \rho dr \quad (8)$$

where  $r_1$  denotes the first minimum of  $g(r)$ , and  $\rho$  is the number density of particles  $N/V$ . To obtain  $g(r)$  it is possible to use OVITO or the LAMMPS compute command `rdf`.

## Extra credit: Defect properties

### 1 Background

Let us now consider some basic defect properties. As discussed in the lectures, the vacancy formation energy gives a strong indication for the importance of many body interactions in a metal. The vacancy formation energy  $\Delta E_f$  (more precisely the *free* energy of defect formation  $\Delta G_f$ ) determines the defect concentration in *equilibrium* according to

$$c = c_0 \exp(-\Delta G_f/k_B T). \quad (9)$$

Please consult the lecture notes on pingpong for more information.

### 2 Tasks

1. Calculate the vacancy formation energy using your potential. Make sure that your result is converged with respect to system size. Compare with a reference value from experiment or first-principles calculations. To this end, find values by literature research or carry out your own DFT calculation(s). Estimate the vacancy concentration at 600 and 900 K assuming  $\Delta G_f \approx \Delta E_f$ . How does the formation energy compare to the cohesive energy? Comment on your result.
2. Compute the migration energy for a vacancy using the nudged elastic band (NEB) method. Based on your results provide an estimate for under which condition one could observe vacancy migration in a molecular dynamics (MD) simulation?

## References

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