



ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Empirical Energy Methods

Lab 1

Atomistic and Quantum Simulations of Materials

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1 Problem 1

The goal of this first exercise is to calculate the lattice constant and the total energy of the face centred bulk of silver by performing some GULP simulations.

The unit cell of the system appears like in Figure 1. There are only four atoms, one at one corner and three at the centre of three faces of the cube. The full system is then obtained by repeating this modular structure along the 3 axis, by setting periodic boundary conditions.

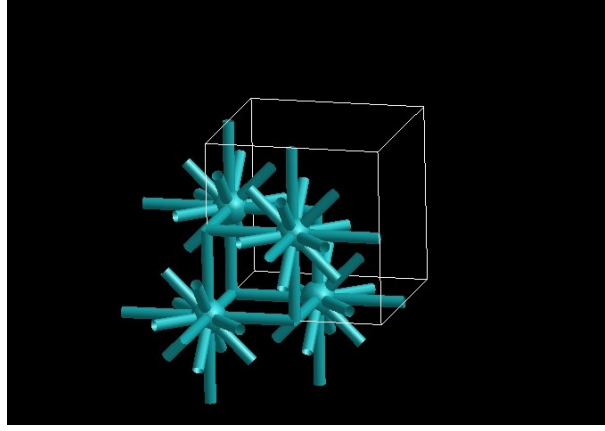


Figure 1: Representation of the unit cell of fcc Ag.

The packing fraction of a unit cell is defined as the percentage of space filled by the particles. In the fcc unit cell there are four particles, then the occupied space can be approximated to the volume of four spheres. Assuming that their radius is such that the one at the corner is in touch with the ones at the face centres, an easy relationship between the radius r and the length of the side of the unit cell a can be found.

$$r = \frac{\sqrt{2}}{2}a \quad (1)$$

$$PF = \frac{V_{occupied}}{V_{cell}} = \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{4}{3}\pi \frac{1}{2\sqrt{2}} \simeq 0.74$$

By taking the ratio between the occupied volume and the volume of the cubic cell, the packing fraction is equal to 0.74 for a generic fcc unit cell. It is not necessary to specify that the element of interest here is silver, indeed this quantity does not depend on the specific element but only on the positions and number of atoms in the unit cell.

1.1 Task 1A

In order to calculate the lattice constant and the total energy of the system described before the definition of a potential which models the interactions between every pair of atoms is necessary. In this first task the 12-6 Lennard-Jones potential has been used.

Two different ways exist in order to calculate what we are interested in. The first one is to use the GULP minimizer which automatically performs relaxations of both the unit cell and the atomic positions. The second one consists in choosing 'manually' different values of the lattice constant near the equilibrium value and calculate the corresponding energy, then the minimum of the energy curve as a function of the lattice parameter will reveal the optimal size of the unit cell. This is done by using the flag 'single' instead of the 'opti' one in the input file.

By following the first procedure the values obtained are 4.0764\AA for the lattice constant, while the angles remained equal to 90° . The corresponding total energy is -11.8784eV .

Then, values of the lattice constant near its equilibrium value (with reference to the first calculation) have been considered, more specifically in the interval $[4.0\text{\AA}, 4.14\text{\AA}]$. By plotting their corresponding total energy, and fitting the data with a polynomial of degree 2, as shown in Figure 2 is possible to understand that it has a quadratic behaviour. The extracted minimum corresponds to 4.0799\AA which is close to the one calculated allowing the structure to relax.

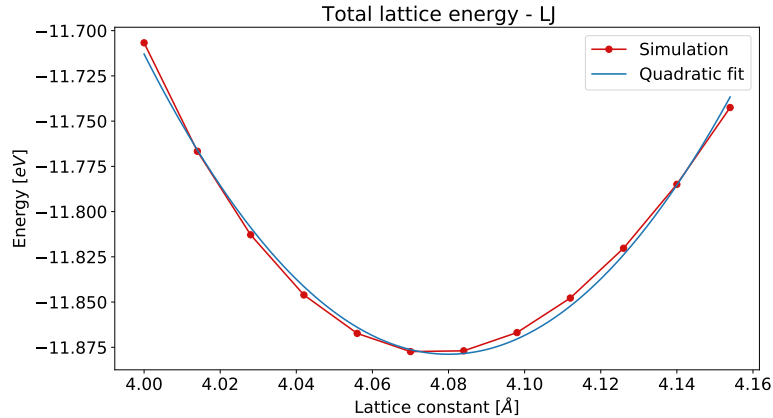


Figure 2: Total energy of the lattice as a function of the lattice parameter and quadratic fit of the data points, by using 12-6 Lennard-Jones potential.

1.2 Task 1B

The same calculations have been repeated by using a different potential, the Embedded Atom Model (EAM), which is not a simple pair-potential but takes into account the number of bonds of each atom to define the energy of a specific interaction. The lattice constant calculated through the first method, which means allowing the relaxation of the structure, has a value of 4.0848\AA and the total lattice energy is -11.8427eV .

The behaviour of the total energy as a function of the lattice constant around the equilibrium value (the same range as before has been used) is showed in Figure 3, and also in this case the best fit is given by a quadratic function, which is caught also better by the data.

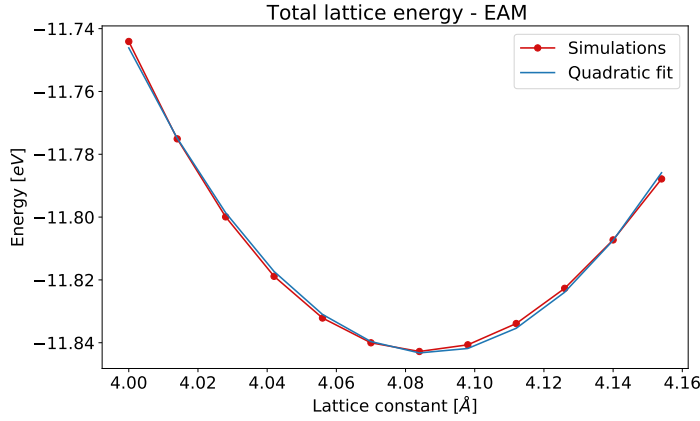


Figure 3: Total energy of the lattice as a function of the lattice parameter and quadratic fit of the data points, by using EAM potential.

This good accordance between the data of the energy obtained from the simulations and the quadratic fit was expected. Indeed, if two atoms are close enough to each other the first derivative of the potential vanishes and they can be modeled by an harmonic oscillator. Then a parabolic fit is appropriate.

It is known that the experimental lattice parameter for Ag is 4.085\AA , which corresponds to the values obtained from the simulations. This good accordance was expected since the structure of the solid we are considering is well described by such potentials. More precisely, the prediction is better for the EAM potential, with a discrepancy of only 0.0002\AA . This is due to the fact that the EAM potential takes into account a more 'sophisticated' effect (explained before) to describe the interaction between two atoms, specifically by adding a term to the usual pairwise one.

As already said, the values obtained for the energy in the calculations with Lennard-Jones and EAM potential are different, but this is justified by the fact that the potentials themselves are different. As a consequence, by modelling the system in two different ways it's possible to capture different features. In particular, more effects are taken into account, more details and precise values are obtained.

2 Problem 2

2.1 Task A

An important property of a crystal is the vacancy formation energy, which corresponds to the energy to remove one atom from it and bring it to infinity, where the energy of an isolated atom is supposed to be zero. In order to calculate this quantity correctly is not possible to only create a vacancy in one unit cell, indeed by doing this too many vacancies would have been created into the system and the total energy would contain also terms which correspond to the interaction between the different vacancies. Then, the creation of a supercell is required, which means to define a new unit cell composed by different small unit cells in all the three directions. The vacancy formation energy strongly depends on the size of the supercell and it converges only when that size becomes large enough, such that two vacancies in two adjacent supercells do not interact anymore.

Here the vacancy formation energy has been studied as a function of the supercell size, by describing the system through a 12-6 Lennard-Jones potential. In particular, different simulations have been run for each supercell size (by only considering cubic supercells due to the symmetry of the system), firstly with all the N atoms, and then by removing one atom of choice (the position of the chosen atom doesn't effect the energy) not allowing the system to relax. Once the energies $E_{i,N}$ and $E_{i,N-1}$ have been collected, Equation 2 gives the vacancy formation energy.

$$E_{f,v} = E_{i,N-1} - \left(\frac{N-1}{N} \right) E_{i,N} \quad (2)$$

As it is possible to see in Figure 4 and in Table 1 the convergence is obtained for a supercell composed by 4 unit cells in all the x, y, z directions, where the adopted threshold for convergence is equal to $0.001eV$.

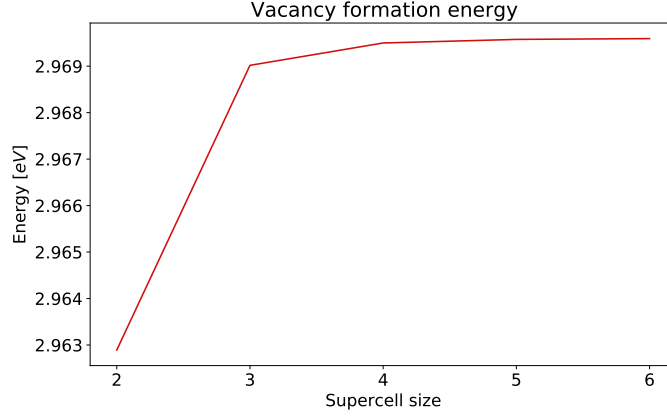


Figure 4: Vacancy formation energy of the lattice as a function of the cubic supercell size by using 12-6 Lennard-Jones potential and not allowing the structure to relax after the removal of the atom.

	$E_{i,N}[eV]$	$E_{i,N-1}[eV]$	$E_{vf}[eV]$
$2 \times 2 \times 2$	-95.0272	-89.0947	2.9628
$3 \times 3 \times 3$	-320.7169	-314.7782	2.9690
$4 \times 4 \times 4$	-760.2178	-754.2787	2.9694
$5 \times 5 \times 5$	-1484.8004	-1478.8613	2.9695
$6 \times 6 \times 6$	-2565.7352	-2559.7960	2.9695

Table 1: Total lattice energy when the supercell has all the N atoms, Total lattice energy when one atom has been removed from the supercell not allowing relaxation, and corresponding vacancy formation energy calculated through Equation 2 for the possible sizes of the cubic supercell (2,3,4,5,6 cells in x,y,z directions) of the system. 12-6 Lennard-Jones potential has been used.

Another important quantity is the cohesive energy, defined as the difference between the bulk energy per atom and the energy of one isolated atom. As already said before, the energy of an isolated atom is assumed to be zero, then the cohesive energy can be simply calculated as the ratio between the total lattice energy and the number of atoms of the lattice, as shown below.

$$E_{coh} = \frac{E_N}{N} \quad (3)$$

For the supercell size calculated before, the ratio between cohesive and vacancy formation energy is equal to -0.9999 , which can be considered equal

to 1. It is exactly what we expect when the system is represented through a Lennard-Jones potential. In this case indeed the energy needed to remove an atom is the energy that keeps the atom bonded to the structure, so the two are the same and the ratio between them is consequently equal to 1, as obtained from the simulations.

2.2 Task B

Now the same simulations are repeated allowing the relaxation of the structure after the creation of a vacancy, which means that once one atom has been removed, the optimal configuration is re-calculated. The obtained values are shown in Figure 5.

	$E_{i,N}[eV]$	$E_{i,N-1}[eV]$	$E_{vf}[eV]$
$2 \times 2 \times 2$	-95.0272	-89.1319	2.9256
$3 \times 3 \times 3$	-320.7169	-314.8193	2.9279
$4 \times 4 \times 4$	-760.2178	-754.3203	2.9278
$5 \times 5 \times 5$	-1484.8004	-1478.9030	2.9278
$6 \times 6 \times 6$	-2565.7352	-2559.8378	2.9278

Table 2: Total lattice energy when the supercell has all the N atoms, Total lattice energy when one atom has been removed from the supercell allowing the relaxation of the structure, and corresponding vacancy formation energy calculated through Equation 2 for the possible sizes of the cubic supercell (2,3,4,5,6 cells in x,y,z directions) of the system. 12-6 Lennard-Jones potential has been used.

If the system can relax after the removal of an atom, its energy becomes lower than when all the atoms are fixed in their positions, indeed the atoms rearrange themselves in order to find the most favourable configuration. In this way, the first term in Formula 2 of the vacancy formation energy is lower, leading also to a smaller difference. The values obtained in this case are then smaller than in the previous case, by not allowing the atoms to relax.

By comparing these results with the experimental value, which is equal to $1.16eV$, a discrepancy is more than evident. The values obtained from the simulations are indeed more than twice the experimental one. This depends on the fact that the Lennard-Jones potential has been used to represent the interactions of the system. A more detailed justification is given in the next Section.

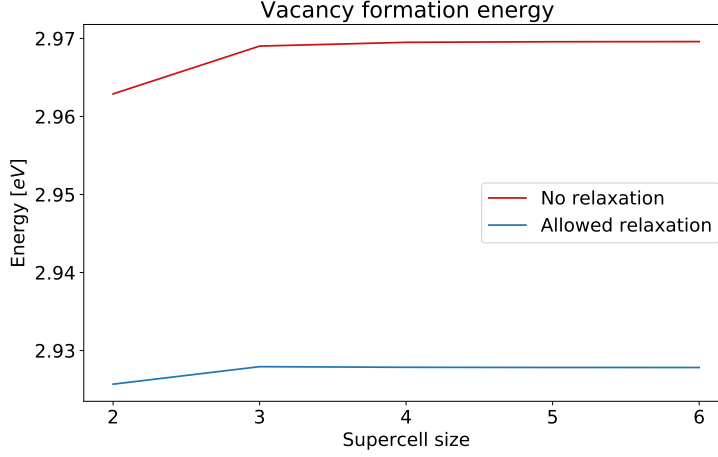


Figure 5: Vacancy formation energy of the lattice as a function of the supercell size by using 12-6 Lennard-Jones potential and allowing/not allowing the structure to relax after the removal of one atom.

2.3 Task C

The same calculations have been performed also by using the EAM potential, firstly by not allowing the relaxation of the structure, and after allowing the structure to relax. The results are showed below. In particular in this case the convergence is already reached for a dimension of 2 unit cells of the supercell.

	$E_{i,N}[eV]$	$E_{i,N-1}[eV]$	$E_{vf}[eV]$	$E_{i,N-1relax}[eV]$	$E_{vfrelax}[eV]$
$2 \times 2 \times 2$	-94.7423	-90.8813	0.9003	-90.8994	0.8822
$3 \times 3 \times 3$	-319.7554	-315.8946	0.90012	-315.9103	0.8843
$4 \times 4 \times 4$	-757.9388	-754.0779	0.90012	-754.0931	0.8849

Table 3: Total lattice energy when the supercell has all the N atoms, total lattice energy when one atom has been removed from the supercell not allowing the relaxation of the structure, and corresponding vacancy formation energy calculated through Equation 2, total lattice energy when one atom has been removed allowing relaxation and respective vacancy formation energy. Each of these for different sizes of the cubic supercell (2,3,4,5,6 cells in x,y,z directions). EAM potential has been used.

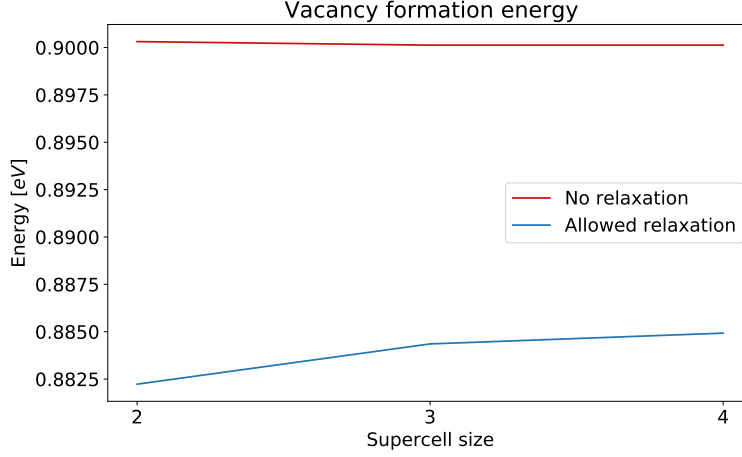


Figure 6: Vacancy formation energy of the lattice as a function of the supercell size by using EAM potential and allowing/not allowing the structure to relax after the removal of one atom.

When the relaxation of the structure is allowed the value of the vacancy formation energy is smaller also in this case, and the motivation is the same as before. In this case the vacancy formation energy is far smaller than by using Lennard-Jones potential and it is also closer to the experimental value, even if in this case it is slightly smaller. This can be justified as follows. The energy approximated through a pair potential doesn't change with the coordination number, indeed it doesn't appear in the respective formula, it's like if it is zero. However, if an atom in a system has a lot of neighbours, when we calculate the potential of the complexive structure there are lots of important terms in the sum, which means that the energy is very low. So, once one atom has been removed all the interactions with its neighbours are removed from the energy, which appears higher than before. As a consequence, the energy to remove an atom is big.

On the other hand, for EAM potential the coordination number is considered in the calculation of the energy, so if the coordination number is big (it is higher than zero), the energy of each atom is smaller in absolute value with respect to the one it would have if a Lennard-Lones potential is used, and the total energy is higher. Then, by going from Lennard-Jones to EAM, the energy of each atom becomes always smaller and so also the vacancy formation energy. This is then why the value obtained in the first case is so high with respect to the experimental value, and the second so low.

$\begin{matrix} \text{slab}[\text{\AA}] \\ \text{vacuum}[\text{\AA}] \end{matrix}$	1	2	3	4	5	6	7
1	3.008e-10	0.0	0.0	2.707e-9	2.137e-16	3.00810e-10	3.008e-10
2	0.0	0.0	0.0	3.008e-10	3.008e-10	6.017e-10	0.0
3	1.805e-9	0.0	3.008e-10	1.5044	0.1570	0.1572	0.1572
4	0.0	0.0	0.0	0.1573	0.1575	0.1575	0.1572
5	0.0	3.008e-10	0.0991	0.1577	0.1579	0.1579	0.1579
6	0.1467	0.1559	0.1575	0.1579	0.1581	0.1581	0.1581
7	0.1468	0.1560	0.1575	0.1580	0.1581	0.1581	0.1581
8	0.1468	0.1560	0.1575	0.1580	0.1581	0.1582	0.1582
9	0.1468	0.1560	0.15759	0.1580	0.1581	0.1582	0.1582
10	0.1468	0.1560	0.1575	0.1580	0.1581	0.1582	0.1582

Table 4: The table shows the values of the surface energy for a system described through 12-6 Lennard-Jones potential and a supercell composed by a layer of vacuum thick as the value of the row and a layer of atoms with thickness equal to the correspondent column.

3 Problem 3

3.1 Task 1 (Mandatory)

Another important quantity that can be studied is the surface energy. Similarly to the vacancy formation energy, it is defined as the cost of creating a surface of the Ag bulk along a crystallographic plane. Also in this case a specific supercell needs to be created, and in particular it has to contain a layer of atoms and a layer of vacuum. This energy depends on two different variables, which are the thickness of the slab and the thickness of the vacuum, that's why it is called also coupled convergence. By performing different GULP simulations of the fcc Ag system with the supercell mentioned before, the surface energy has been calculated through Equation 4.

$$\gamma_{slab} = \frac{E_{slab} - NE_{bulk}}{2A_{slab}} \quad (4)$$

The obtained values for γ_{slab} , by using the 12-6 Lennard-Jones potential are showed in Table 4. It is possible to see that, if a threshold of $0.001eV$ is adopted, the surface energy converges for a slab of thickness of 6\AA and a layer of vacuum of 4\AA (which corresponds to a value for the energy equal to $0.1575eV$).

It's possible to deduce that if a surface is created at less than 4\AA from another one, then strong interactions will be present between the two. The same is for a layer of atoms not enough thick (smaller than 6\AA), the two surfaces which are delimiting it are interacting and they affect strongly the energy of the system. Only when the created surfaces don't feel each other

anymore, because they are enough far away, the convergence is obtained and the energy stabilizes.

Note: the values showed in Table 4 have been obtained by using in the input file an hypotized lattice constant of 4.080\AA instead of the one found in Problem 1. However, due to the fact that the calculations have been performed with the 'opti' flag, and so the optimized structure is re-calculated automatically during the simulation, the results are the same as if the value from Problem 1 would have been used.

3.2 Task 2 (Optional)

When the system is modeled through the EAM potential, the values obtained for the surface energy are the ones reported in Table 5. In this case the convergence is obtained for a thickness of only 2\AA for both slab and vacuum.

$\begin{matrix} \text{slab}[\text{\AA}] \\ \text{vacuum}[\text{\AA}] \end{matrix}$	1	2	3	4	5	6	7
1	1.9481e-8	0.0444	0.0	0.0	5.993e-10	2.996e-10	8.989e-10
2	0.0447	0.0444	0.0443	0.0442	0.0442	0.04418	0.04415
3	0.0447	0.0444	0.0443	0.0442	0.0442	0.04418	0.04415
4	0.0447	0.0444	0.0443	0.0442	0.0442	0.04418	0.04415
5	0.0447	0.0444	0.0443	0.0442	0.0442	0.04418	0.04415
6	0.0447	0.0444	0.0443	0.0442	0.0442	0.04418	0.04415
7	0.0447	0.0444	0.0443	0.0442	0.0442	0.04418	0.04415
8	0.0447	0.0444	0.0443	0.0442	0.0442	0.04418	0.04415
9	0.0447	0.0444	0.0443	0.0442	0.0442	0.04418	0.04415
10	0.0447	0.0444	0.0443	0.0442	0.0442	0.04418	0.04415

Table 5: The table shows the values of the surface energy for a system described through EAM potential and a supercell composed by a layer of vacuum thick as the value of the row and a layer of atoms with thickness equal to the correspondent column.

The EAM potential, as already said before, models the interactions more accurately, more specifically they have a lower energy because of the presence of other bonds is considered. So, also the interactions between the surfaces are better described and due to their nature they disappear at a shorter distance.

4 Problem 4

The result of a simulation strictly depends on the choice of the potential used to modelize the interactions between the atoms. The Lennard-Jones potential is a pairwise potential, which involves only two atoms at a time and describes a weak interaction due to the instantaneous dipole-dipole attraction. Consequently, this kind of potential is suitable only for systems which can be described by weak interactions with a short attractive term, like electronically neutral atoms or molecules, noble gases and methane. It cannot predict accurately crystal structures in metals or covalent solids.

In a structure modelized through this potential one bond doesn't know anything about the others, indeed there is a lack of environment-dependence. Then Lennard-Jones potential can be used when some properties which do not depend on the environment of the atoms are needed.

On the other hand, the Embedded Atom Model considers the number of bonds of one atom and models its energy depending also on that, in particular by adding an additional term to a pair-potential term. Indeed the main physical property of EAM is the moderation of bond strength by other bonds (coordination-dependent bond strength). Then EAM is suitable for metallic systems.

So, depending on the properties of interest and the system studied, different types of potentials are needed to obtain an appropriate degree of accuracy. Both the potentials mentioned before are not able to describe charged systems in an appropriate manner, indeed in this type of systems long-range interactions are present and they cannot be caught by short-range potentials like Lennard-Jones and EAM, more complicated forms are needed to get accurate results.

Another example of empirical potential that can be used in GULP calculations is the Axilrod-Teller potential. It is a three-body potential able to capture the instantaneous induced dipole-induced dipole interactions.

$$V_{ijk} = E_0 \left[\frac{1 + 3 \cos \gamma_i \cos \gamma_j \cos \gamma_k}{(r_{ij} r_{jk} r_{ik})^3} \right] \quad (5)$$

where V is the ionization energy. It results from a third-order perturbation correction to the attractive London dispersion interactions. Due to the fact that ionic solids have a three-centre dispersion contribution, and then three-body forces are present, this potential is a good choice to describe such type of systems.

5 Problem 5

By deriving the equation of the Lennard-Jones potential and impose it to be equal to zero, the minimum is found to be equal to:

$$r_0 = \sigma = 2.644\text{\AA} \quad (6)$$

In Problem 1 we obtained that, by using the 12-6 Lennard-Jones potential, the lattice constant was equal to 4.0764\AA . Is it then possible to calculate the distance between each pair of atoms by simple geometry calculations.

$$d = \frac{1}{\sqrt{2}}a = 2.88249\text{\AA} \quad (7)$$

where a is the lattice constant. By comparing these two results, it appears that the distance between every pair of atoms in the unit cell obtained from the simulation is larger than sigma. This discrepancy can be explained by the fact that when we simulate a system of atoms (unit cell with periodic boundary conditions) we don't have a single Lennard-Jones potential, but a sum of different LJ potentials, one for all the possible pairs of atoms and we have to take the minimum of it, which implies to go through a more complicated calculation and a different result. Apparently, a potential of an entire system has an equilibrium distance between two atoms slightly larger than the one for a single pair of atoms.

6 Problem 6

The goal now is to set up for scratch a calculation for gold-copper alloy (CuAu) in the $L1_0$ structure.

6.1 Task A

First of all, in order to create the needed input file, it's necessary to know the structure of this system and the simplest unit cell of the bulk. The literature reveals it has a face-centred tetragonal lattice, with alternating planes of Au and Cu atoms in $[001]$ direction. Then, the simplest possible unit cell for the bulk is made by only two atoms, one of Cu and one of Au, as shown in Figure 7.

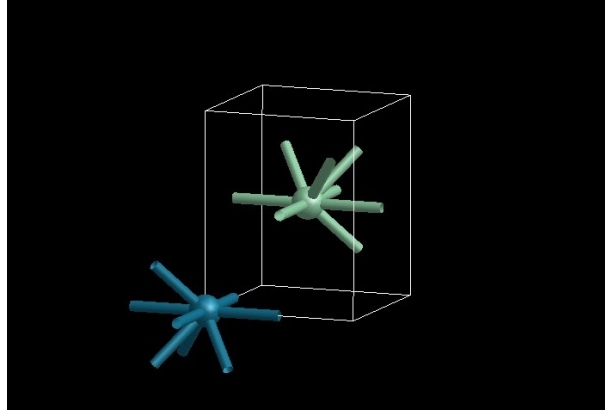


Figure 7: Representation of the unit cell of CuAu alloy.

The sides of the cell are still orthogonal but the cell is not cubic anymore, indeed the new lattice parameters are $a = 2.864\text{\AA}$, $b = 2.864\text{\AA}$ and $c = 3.662\text{\AA}$.

Then, by knowing the A and B coefficients for Au and Cu, it is possible to calculate the A and B coefficient for a 12-6 LJ potential for AuCu by using Equation 9.

$$\begin{aligned} A_{Au} &= 214180.20 \\ B_{Au} &= 625.482 \\ A_{Cu} &= 3000.00 \\ B_{Cu} &= 18.00 \end{aligned} \tag{8}$$

$$\begin{aligned} A_{ij} &= \sqrt{A_i A_j} \\ B_{ij} &= \sqrt{B_i B_j} \end{aligned} \tag{9}$$

By substituting the values we obtain, for the interactions between an atom of Au and an atom of Cu, the following parameters for the Lennard-Jones potential:

$$\begin{aligned} \bar{A} &= \sqrt{A_{Au} A_{Cu}} = \sqrt{214180.20 \cdot 3000.00} = 25348.3845 \\ \bar{B} &= \sqrt{B_{Au} B_{Cu}} = \sqrt{625.482 \cdot 18.00} = 106.1069 \end{aligned} \tag{10}$$

At this point the input file can be written to start the calculation for bulk CuAu. It looks like Figure 8.

```

opti dist comp conp
cell
    2.864 2.864 3.662 90 90 90
fractional 2
Au      0.000000000 0.000000000 0.000000000
Cu      0.500000000 0.500000000 0.500000000
lennard 12 6
Au Au 214180.200 625.482 0.000 40.000
Cu Cu 3000.000 18.000 0.000 40.000
Au Cu 25348.3845 106.1069 0.000 40.000

```

Figure 8: Input file for the simulation of CuAu by using 12-6 Lennard-Jones potential.

6.2 Task B

The GULP calculation, by using the implemented input file, optimizes the CuAu structure by finding an optimum value for the lattice parameters which are different from the initial one.

	Initial value	Optimized value
a	2.864	3.008667
b	2.864	3.008667
c	3.662	3.008325
Volume	30.03754	27.231588

As it is possible to see, the optimized values of the lattice parameters for the system are different from the ones found in the literature (and used for the implementation of the input file). This is due to the fact that, as explained before in Problem 4, the simulation is considering an entire system of atoms and not only a pair of them as in a single unit cell. As a consequence, from the large number of interactions between each pair of atoms a much more complicated potential arises and the atomic positions are not anymore the same.

6.3 Task C

In the paper [1] an EAM potential which is able to describe both fcc monoatomic metals and fcc alloys is described. In particular, the equations that describe the model contain the term $F(\rho_i)$ which is the energy to embed an atom i in an electron density ρ_i . It is not a pair-potential term because it depends on the electron density of the atom i which is obtained by summing all the electron densities (due to all the other atoms) at its position. This term then

takes into account many-body effects. As already said, the F term depends on ρ and if the assumption that only the nearest neighbours contribute to its value is made, then for the considered fcc lattice it is possible to approximate the expression to the following one.

$$\rho_i = \sum_{\substack{\text{neighbours} \\ j \neq i}} f(r_{ij}) = 12f(r) \quad (11)$$

where $f(r)$ has the same expression of the Equation (4) in the paper.

In a monoatomic crystal with N atoms the energy can be easily defined as $E_{tot} = NE$, where

$$E = F(\rho) + \frac{1}{2} \sum_m \phi(r_m) \quad (12)$$

Indeed, due to the fact that all the atoms are equal, if E_i represents the energy of one of them, E_{tot} can be written as the sum of such N energies. In addition, $F(\rho)$ depends on the electronic density in one spot, but thanks to the periodic boundary conditions all the spots are equal. The same for the pair-potential term $\phi(r_m)$.

$$\begin{aligned} E_{tot} &= \sum_{i=1}^N E_i = \sum_{i=1}^N \left[F(\rho) + \frac{1}{2} \sum_m^{\text{neighbours}} \phi(r_m) \right] \Big|_i \\ &= \sum_{i=1}^N F(\rho) + \sum_{i=1}^N \left[\frac{1}{2} \sum_m^{\text{neighbours}} \phi(r_m) \right] \\ &= NF(\rho) + N \left[\frac{1}{2} \sum_m^{\text{neighbours}} \phi(r_m) \right] = \\ &= N \left[F(\rho) + \frac{1}{2} \sum_m^{\text{neighbours}} \phi(r_m) \right] = NE \end{aligned} \quad (13)$$

6.4 Task D (Optional)

If the assumption of Task C is made, the model for the energy built by R.A.Johnson and described in [1] gives the following curve for the energy.

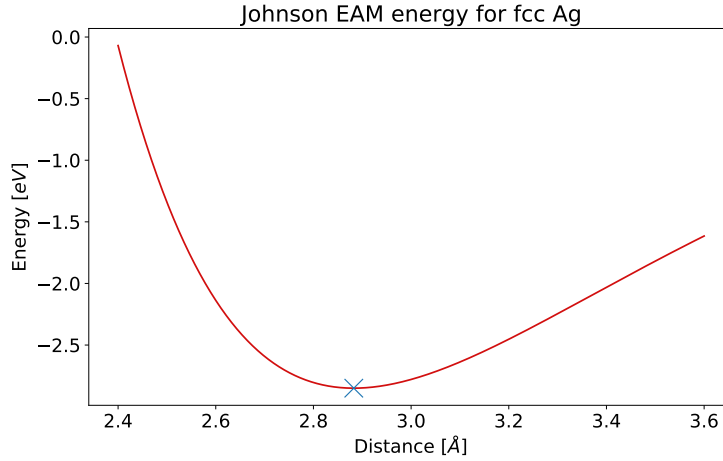


Figure 9: Johnson EAM energy from [1] as a function of the distance between two atoms.

As it is possible to see, the curve shows a repulsive behaviour at very short distances, representative of the electronic repulsion, and an attractive one at relatively long distances, while a minimum is present at 2.882641\AA , so it has the same behaviour of the potentials already seen, as expected. This last value represents the optimal distance between two neighbour atoms modeled with this potential. It can be then compared to the optimal distance for a Lennard-Jones model, as the one found in Problem 5 from the data collected in Problem 1, which was 2.882491\AA . It's possible to understand that by considering the electronic density present in the vicinity of an atom in order to modelize its interactions, the energy of the bonds is smaller (in absolute value) than by not considering it, so that the atoms tend to stay less close to each other and the equilibrium distance between nearest neighbour atoms is slightly bigger than by using a Lennard-Jones potential, where the bonds have all the same energy. In this case, the two values are really close to each others, so it means that the electronic density is not severely affecting the strength of the bonds.

7 Problem 7

This last section is dedicated to the calculation of the bulk modulus of fcc Ag, by using first the 12-6 Lennard-Jones potential and then the EAM one. The bulk modulus is a property of a system defined as its resistance to compression, so that it is necessarily related to thermodynamic quantities

such as volume and pressure through the equation of state. In order to find the value of the bulk modulus for fcc Ag it is possible to plot again the total lattice energy, but this time as a function of the volume, and perform a fit of the data through the curve described by Equation 14.

$$E = E_0 + \left(\frac{9}{8}\right) B_0 V_0 \left[\left(\frac{V_0}{V}\right)^{2/3} - 1 \right]^2 + \left(\frac{9}{16}\right) B_0 V_0 (B'_0 - 4) \left[\left(\frac{V_0}{V}\right)^{2/3} - 1 \right]^3 \quad (14)$$

By finding the analytical expression of the curve that best fits the energy values is possible to know the bulk value of the structure.

A range of points around the equilibrium point of the system has been used, and their energies collected so that the following graphs have been obtained.

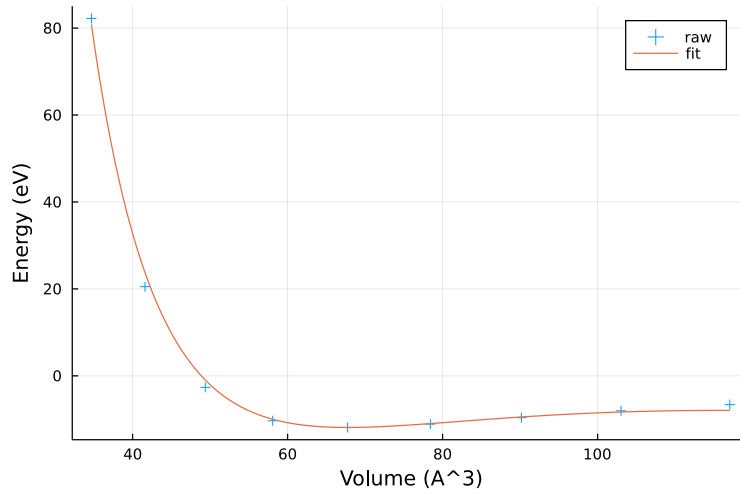


Figure 10: Computed values of the total lattice energy as function of the volume of the unit cell, and fit with the curve of Equation 14. The potential used is 12-6 Lennard-Jones potential.

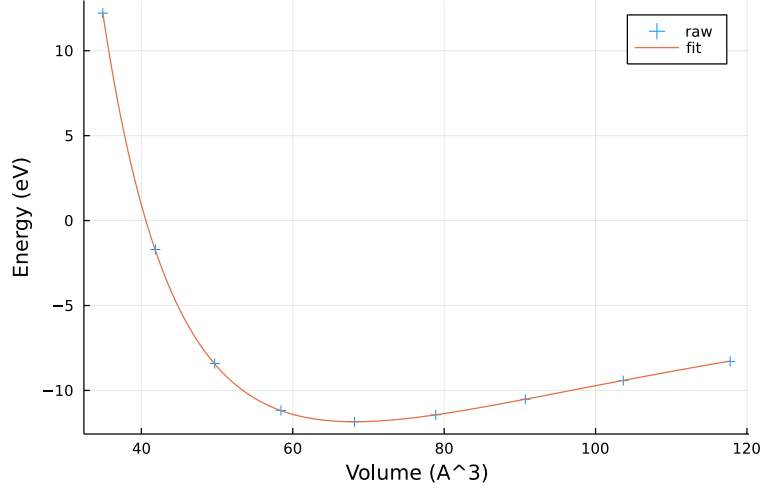


Figure 11: Computed values of the total lattice energy as function of the volume of the unit cell, and fit with the curve of Equation 14. The potential used is EAM potential.

By using the 12-6 Lennard-Jones potential the value of the bulk modulus which gives the best fit of the data appears to be $B_{0,LJ} = 1.7105eV/A^3 = 274.061GPa$.

While if the system is described through the EAM potential its value becomes much smaller, almost less than half of before: $B_{0,EAM} = 0.67268eV/A^3 = 107.776GPa$.

By referring to the paper [2] the experimental value, with some justified corrections, for the bulk modulus of fcc Ag can be considered equal to $103.8GPa$, while the most accurate found through the use of complicated functionals is $110.2GPa$. Then the first result obtained here, through the use of the 12-6 Lennard-Jones potential is not at all accurate, which means that this type of potential is not able to capture the elastic properties of the system always due to the fact that takes into account only pairwise interactions between the atoms. The use of the EAM potential instead lets to predict quite accurately the values of B_0 , indeed it is in the middle between the experimental value and the one found in the literature. This means that an elastic property, like the resistance to compression, strongly depends on the many-body effect taken into account by the EAM potential.

References

- [1] R. A. Johnson *Alloy models with the embedded-atom method*, Physical Review B, 39, 12554, Num-17, 15 June 1989-I
- [2] Patanachai Janthon, Sijie (Andy) Luo, Sergey M. Kozlov, Francesc Vines, Jumras Limtrakul, Donald G. Truhlar and Francesc Illas, *Bulk Properties of Transition Metals: A Challenge for the Design of Universal Density Functionals*, J. Chem. Theory Comput. 2014, 10, 3832-3839