Project 1

Introduction

Density-functional theory (DFT) is a computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure (principally the ground state) of many-body systems. CASTEP (**CA**mbridge **S**erial **T**otal **E**nergy **P**ackage) is a shared-source academic and commercial software package utilising DFT with a plane wave basis set to run ab-initio calculations of the electronic properties of materials.

Starting from the many-body wavefunction, the Born–Oppenheimer approximation is employed where the nucleus is considered as static. Using Bloch's Theorem a wavefunction with a cell-periodic factor and a phase factor so that the basis functions are orthogonal and it is easy to perform a Fourier transform from real to reciprocal space and vice versa. Along with plane waves and iterative diagonalisation methods (via conjugate gradient or blocked Davidson algorithms), pseudopotentials are essential to the CASTEP code for reducing the computational expense of the calculation. Pseudopotentials replace the atomic nucleus and the core electrons by an effective numeric potential.

$$i\frac{\partial}{\partial t}\Psi(\{\mathbf{r}\},t) = \left[\sum_{j=1}^{N} \left(-\frac{1}{2m_j}\nabla^2 + v(\mathbf{r}_j) \right) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} u(\mathbf{r}_i,\mathbf{r}_j) \right] \Psi(\{\mathbf{r}\},t)$$

Equation 1: Many body Schrödinger equation

Direct methods for solving the Schrodinger equation are based on the expansion of Slater determinants. Hartree-Fock and post-Hartree-Fock methods require huge computational efforts and are virtually impossible with more complex systems. As such, using DFT, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function. In the case of DFT, these are functionals of the spatially dependent electron density.

$$n(\mathbf{r}) = N \int d^3\mathbf{r}_2 \cdots \int d^3\mathbf{r}_N \, \Psi^*(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N).$$

Equation 2: Density

The major problem with DFT is that the exact functionals for exchange and correlation are not known, except for the free-electron gas.

$$E_{\mathrm{XC}}^{\mathrm{LDA}}[n] = \int \varepsilon_{\mathrm{XC}}(n)n(\mathbf{r}) \, d^3\mathbf{r}.$$

Equation 3: Exchange correlation

However, approximations exist which permit the calculation of certain physical quantities quite accurately. One of the simplest GGA (generalised gradient approximation) is the local-density approximation (LDA), where the functional depends only on the density at the coordinate where the functional is evaluated. The Perdew-Burke-Ernzerhof (PBE) functional is also commonly used as it is a non-empirical functional with reasonable accuracy over a wide range of systems.

The basic steps in a DFT calculation are: 1) defining the system and its boundaries, 2) selecting a functional (i.e LDA or PBE), 3) solving the Kohn-Sham equations (a set of coupled equations that describe the electronic structure) to obtain the electronic density and energy of the system, and 4) using the obtained electronic density to calculate other properties of the system, such as forces, charge density, and dipole moments.

Method:

In this project, the phase stability of Al, Si and Ti are calculated in four different cubic crystal structures: sc (simple cubic), bcc (body-centered cubic), and fcc (face-centered cubic), diamond. Then the bandstructures of fcc-Al, fcc-Si, fcc-Ti are calculated at their equilibrium lattice parameter by calculating the energy against k in reciprocal space. By plotting graphs of energy vs lattice parameter, the structure with the EV-curve of the lowest energy per atom can be identified to be the most stable. CASTEP calculated the internal energy for a primitive unit cell. The primitive unit cell sc, fcc and bcc contain 1 atom each. Only the diamond primitive unit cell contains 2 atoms as such the internal energies halved and plotted with the other structures.

The relative stability of AlSi and AlTi in four different crystal structures: rocksalt (NaCl), Zincblende (ZnS), Ceasium Chloride (CsCl), and L1o (CuAu) is also examined to determine the most stable crystal structure and the heat of formation of AlSi and AlTi. The equation involving internal energies of Al, Si and Ti in their most stable state is used to determine the heat of formation:

$$\Delta H(\text{AlSi}) = E_{\text{tot}}(\text{AlSi}^s) - \frac{1}{2}\left[E_{\text{tot}}(\text{Si}^s) + E_{\text{tot}}(\text{Al}^s)\right]$$

Equation 4: Heat of formation of AlSi

$$\Delta H(\text{AlTi}) = E_{\text{tot}}(\text{AlTi}^s) - \frac{1}{2}\left[E_{\text{tot}}(\text{Ti}^s) + E_{\text{tot}}(\text{Al}^s)\right]$$

Equation 5: Heat of formation of AlTi

For crystal structures of elements that were not given, the EV curves were plotted and a 4th order polynomial is fitted to find the equilibrium lattice parameter (eqm_a) and the code was run again with the eqm_a. Object oriented programming was used to accelerate code development for this project due to repeated similar calculations.

Results

The results of minimum energies and lattice parameters are detailed below. The CASTEP method of calculating lattice parameters was verified as 3.9 and 5.43 Å for fcc and diamond-Silicon and it agreed with the literature.

Element/structure (a)	Al	Si	Ti
SC	2.7	2.5	2.6
FCC	3.2	3	3.2
BCC	4	3.8	3.9
Diamond	5.8	5.4	5.6

Table 1: Lattice parameters (a) for Al, Si and Ti in sc, fcc, bcc and diamond crystal structures

Alloy/structure (a)	AlSi	AlTi
Rocksalt	5.1	5.1
Zincblende	5.6	6
Ceasium Chloride	3.1	3
L1o	2.8	2.9

Table 2: Lattice parameters (a) for AlSi and AlTi in rocksalt, zincblende, ceasium chloride and L1o crystal structures

Element/structure (int E)	Al	Si	Ti
SC	-109.258	-168.621	-1590.257
FCC	-109.737	-168.509	-1591.171
BCC	-109.723	-168.711	-1590.924
Diamond	-108.986	-169.022	-1588.673

Table 3: Minimum internal energies (int E) for Al, Si and Ti in sc, fcc, bcc and diamond crystal structures

Alloy/structure (int E)	AlSi	AlTi
Rocksalt	-278.258	-1700.452
Zincblende	-277.918	-1697.800
Ceasium Chloride	-277.852	-1701.476
L1o	-278.479	-1701.832

Table 4: Minimum internal energies (int E) for AlSi and AlTi in rocksalt, zincblende, ceasium chloride and L1o crystal structures
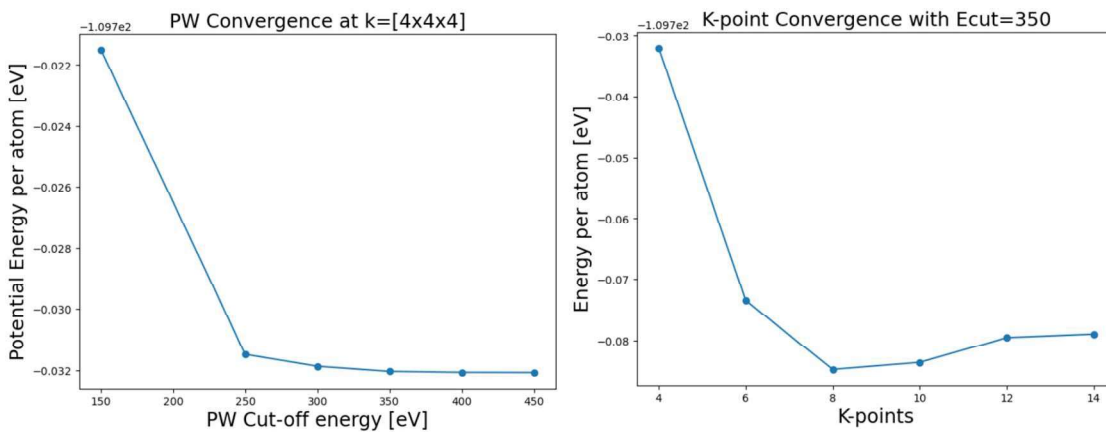
Figure 1: ECut and K-points convergence

Relative stability

The relative stabilities can be seen by plotting the energy per atom curves.
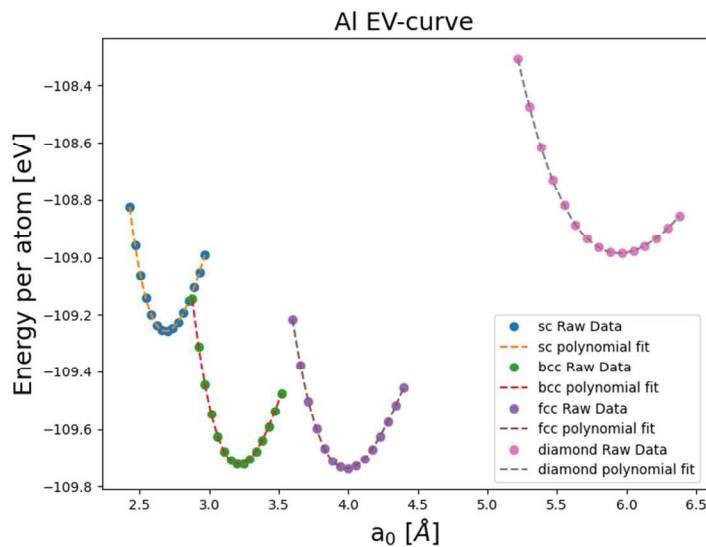
Figure 2: Al E-V curve

From the figure, BCC and FCC have minimum energies that are close together but FCC has the lower minimum energy. As such Al takes the form of FCC which is consistent with experiment.
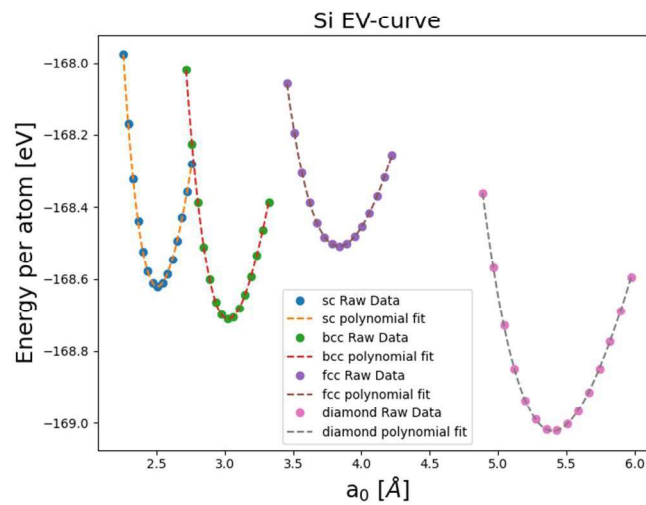

Figure 3: Si E-V curve

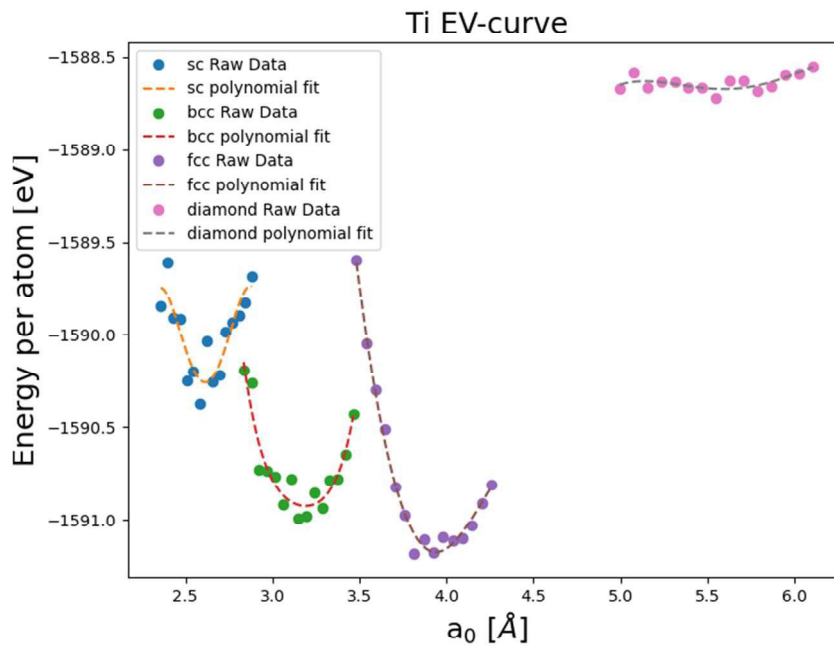For Si, the diamond structure results in the lowest energy per atom.

Figure 4: Ti E-V curve

For Ti, the FCC structure results in the lowest energy per atom.

Bandstructures

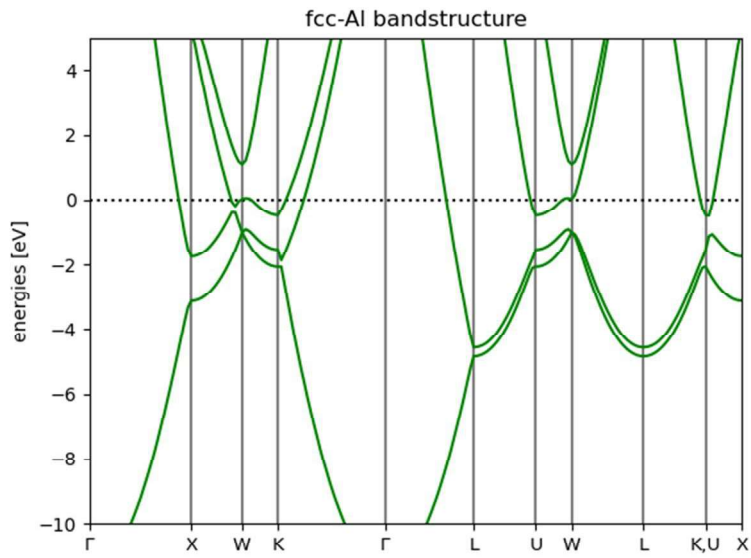The bandstructures were calculated at Ecuts of 350 and kpts of (12,12,12).

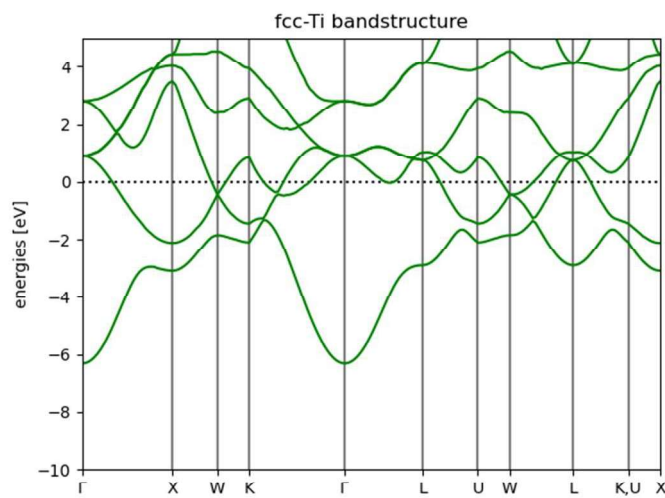Figure 5: fcc-Al bandstructure
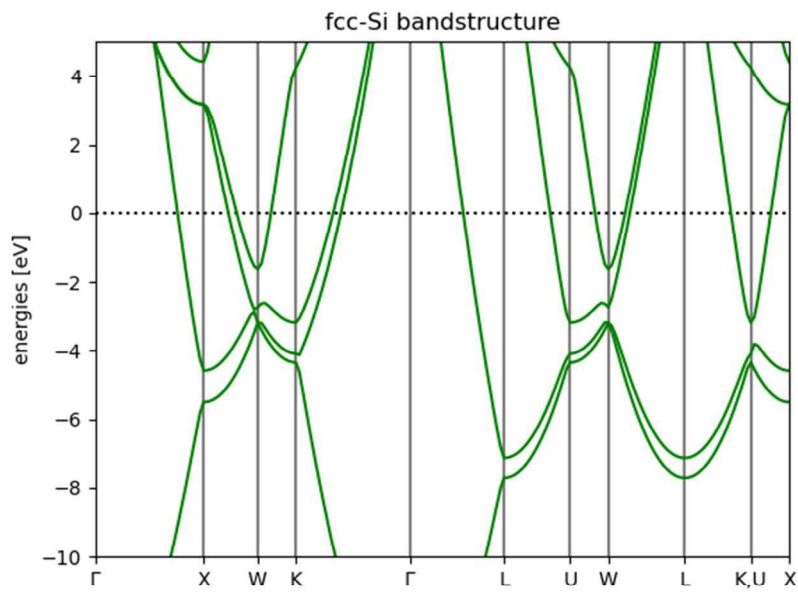
Figure 6: fcc-Si bandstructure

Figure 7: fcc-Ti bandstructure

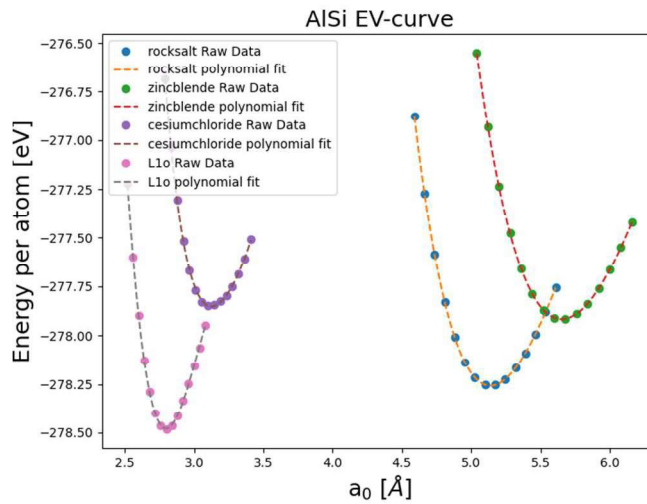None of the element's have bandstructures that exhibit semiconducting properties.
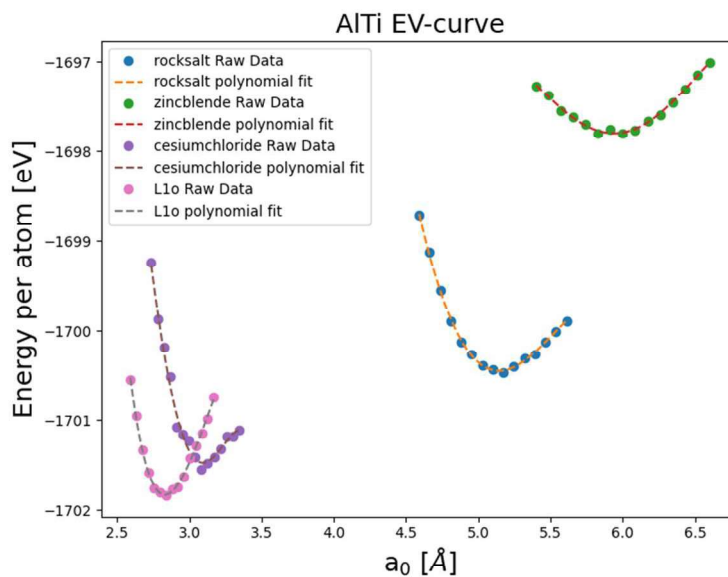

Figure 8: AlSi E-V curve

Figure 9: AlTi E-V curve

For both AlSi and AlTi, the L1o structure results in the lowest energy per atom.

Structures	Internal Energies	Heat of formation
fcc-Al	-109.7	not calculated
diamond-Si	-169	not calculated
bcc-Ti	-1590.9	not calculated
L1o-AlSi	-278.5	-139.1
L1o-AlTi	-1701.8	-851.5

Table 10: Heat of formation in kJ/mol

Discussion

Relative stabilities

The relative stabilities of elements and alloys are not determined by the lattice parameter but are much more likely due to how close atoms are together and the strength of the bonds created. There is an interplay of the attraction between the nuclei and the sea of delocalised electrons but also the repulsion of nuclei. CASTEP calculates the energies which encompasses all of these interactions.

Heat of formation
The heat of formation of AlTi is much greater than AlSi as the internal energy of Ti is much greater than that of diamond Si. This is due to the electronic configuration of Ti as it has many delocalised electrons resulting in very strong metallic bonds. From equation 5, the internal energy of the constituent elements contributes greatly to the heat of formation as the bonds of Ti have to be overcome first before forming the alloy.

Bandstructure discussion
The Ecut was run at 350eV and kpts at (12,12,12), the results were converged with respect to the basis-set and Brillouin zone sampling. As fcc-Si is not the most stable crystal structure, it can be concluded that crystal structure diamond which is the most stable and used in industry is responsible for the semiconducting properties. The fcc-Si and fcc-Al bandstructures are very similar as they have the same electronic configuration. The fcc-Ti bandstructure is very different to the other two as the conduction electrons are more shielded. By observation, the peaks in the bandstructures of fcc-Al and fcc-Si are much more narrow, meaning the 2nd derivatives are much greater. As such, the effective mass of the electrons in fcc-Al and fcc-Si is much lower than that of fcc-Ti.

AlSi and AlTi discussion
L1o is a tetragonal distortion of the fcc structure. The atoms are at the positions of a face centered cubic lattice when c = a. Indium (A6) has a related structure. The L1o crystal structure was the most stable for AlSi and AlTi. This is likely due to the misfit between the Al, Si and Ti atoms distorting the lattice. This tetragonal distortion usually results in increased in yield strength.

Error Analysis:
Any errors would arise from incorrect fitting parameters or insufficient convergence with ECut and kpoints.

Outlook on using CASTEP in a broader multiscale modelling approach

The relative stabilities provides information on the crystal structure materials occupy which dictates many material properties that can be explored up the length scale with molecular dynamics. The bandstructures calculated provide information on the electrical properties of materials. This can be a method to screen for materials. The heat of formation provides information that can be used in CALPHAD approaches. By using CALPHAD to study what phases are stable via different processing routes, each phase can be screened using CASTEP for desired properties. ESPEI is a software package designed to create CALPHAD databases by combining experimental data and density functional theory methods such as CASTEP. The movement of information up and down the length scales allows for a rigorous exploration of materials for scientific and engineering purposes.

Summary and conclusion

This project calculated relative stabilities of Al, Si, Ti, AlSi and AlTi determining that the most stable structures were fcc, diamond, fcc, L1o and L1o respectively. By calculating the bandstructures of fcc-Al,Si and Ti, all indicated conducting properties. Effective mass of electrons were also qualitatively inferred by analysing the width of the peaks. The heat of formation was also calculated.

Project 2

An introduction encompassing a brief description of the modelling method, its underlying theory and how it is implemented on a computer. [7]

Molecular dynamics (MD) is a computational method typically used in material science, biophysics and chemical physics for analysing the time dependent movements of atoms and molecules. Using the Verlet algorithm, positions and velocities of particles at previous time steps to calculate their new positions with Newton's equations of motion. Next, the interatomic potentials and molecular force fields, forces and potential energies are numerically calculated to determine the trajectories of atoms and molecules.

Due to the many body nature of complex molecular systems, analytically determining the properties is impossible. MD simulation circumvents this problem by making use of statistical mechanics, using numerical methods and minimising errors by appropriate choice of algorithms and parameter optimisation. This allows MD simulation to be used to determine the macroscopic thermodynamic properties of the system studied. Time averages of an ergodic system are equivalent to the microcanonical ensemble averages.

This project demonstrates the effectiveness of MD in calculating materials properties such as the specific heat (cp), internal energy and radial distribution functions (RDFs) for Aluminium (Al) and Copper (Cu). The data is then used to determine the melting point of the material.

Method:

Firstly, the code was run to find the most stable structures of Aluminium (Al) and Copper (Cu). Next, the convergence was found for the cp, internal energy and RDFs for Al and Cu with the number of atoms and time steps. Finally, using the convergence parameters, the cp, internal energy and RDFs were calculated for a range of temperatures. By analysing where the cp spikes and the gradient of the internal energy changes, the melting point is determined.

Results:

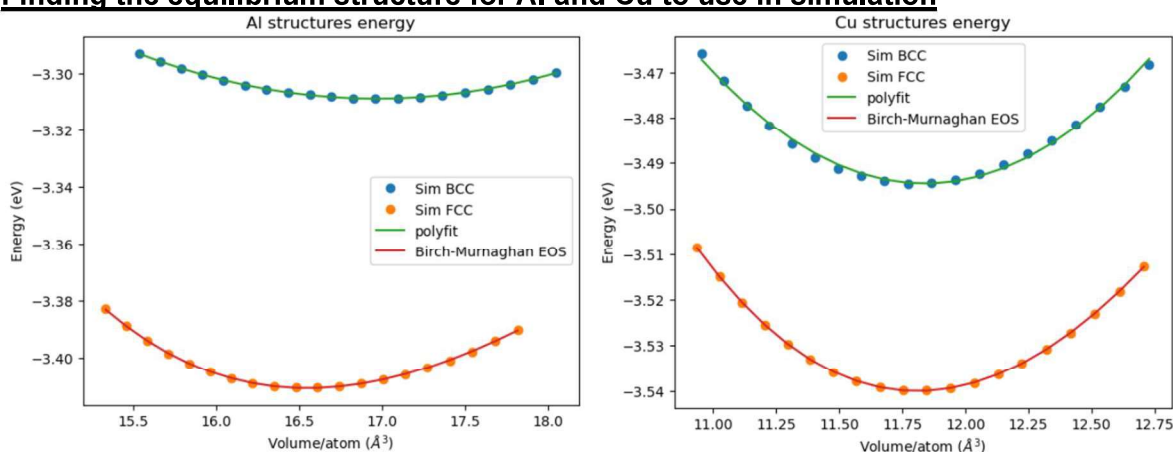**Finding the equilibrium structure for Al and Cu to use in simulation**

Figure 1: Relative stabilities of Al and Cu

The lattice parameters for fcc-Al and fcc-Cu were calculated to be 4.045Å and 3.61Å which is in agreement with the literature.

Convergence of cp, internal energy and RDF with atoms and timesteps
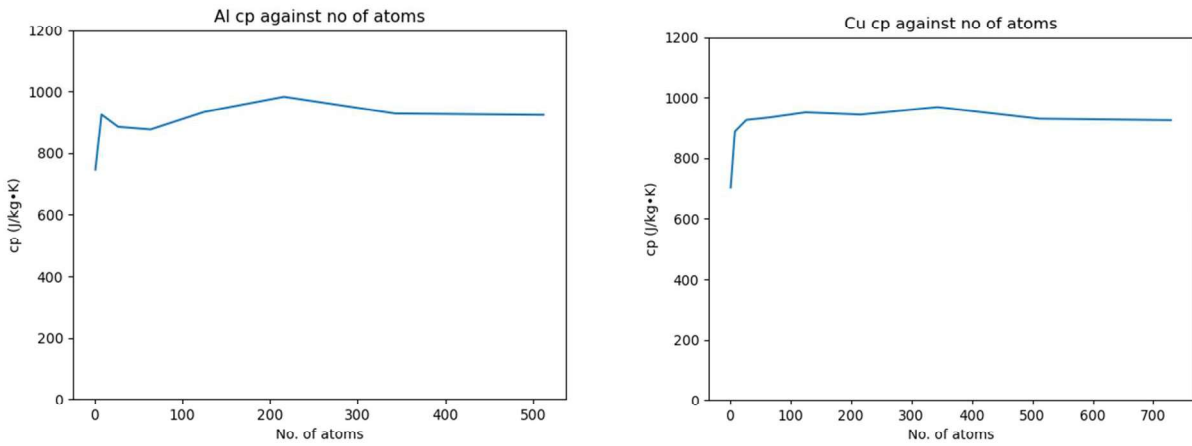
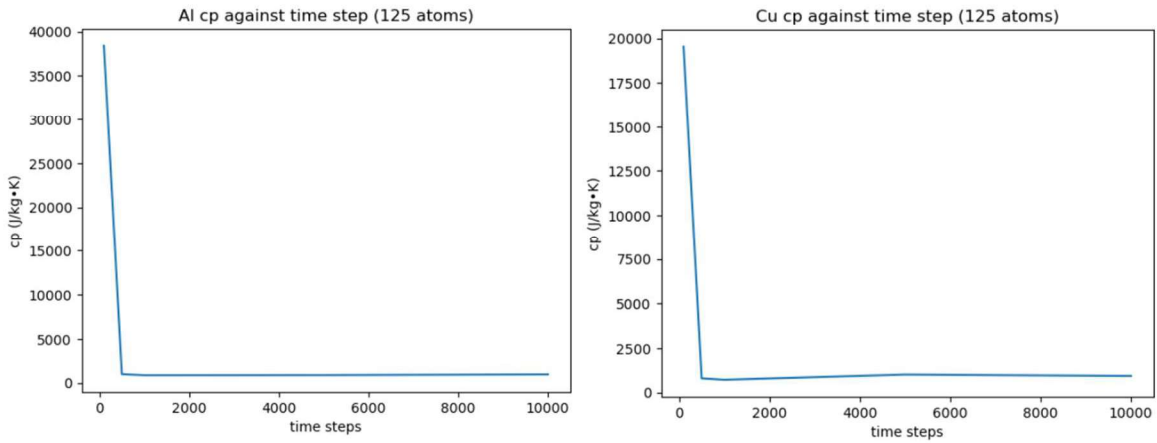Figure 2: Convergence of cp against no. of atoms for Al and Cu

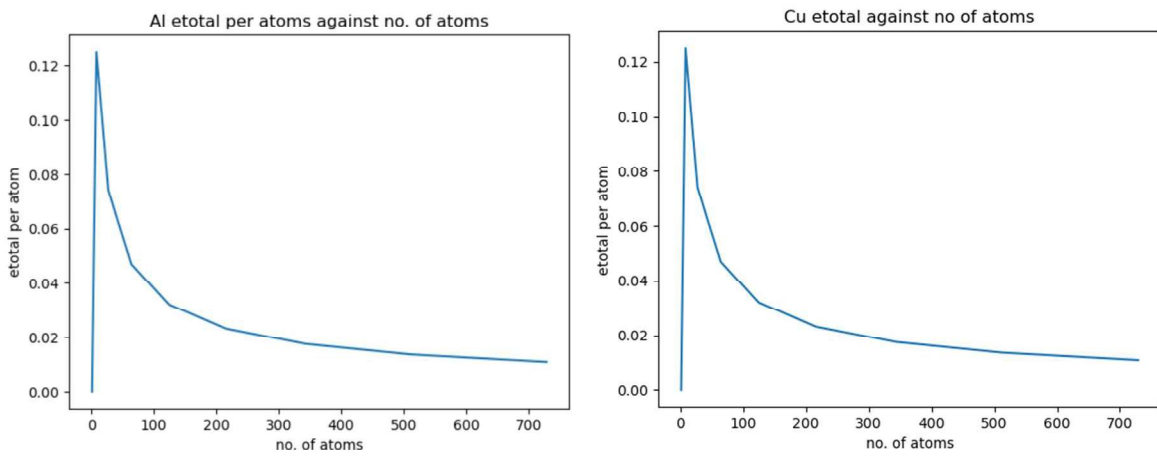Figure 3: Convergence of cp against time step for Al and Cu

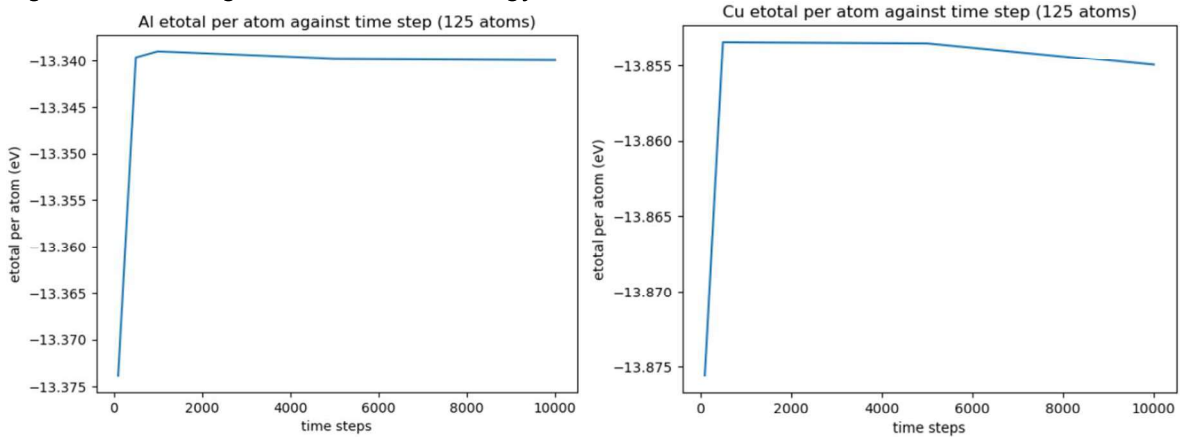Figure 4: Convergence of internal energy with number of atoms for Al and Cu

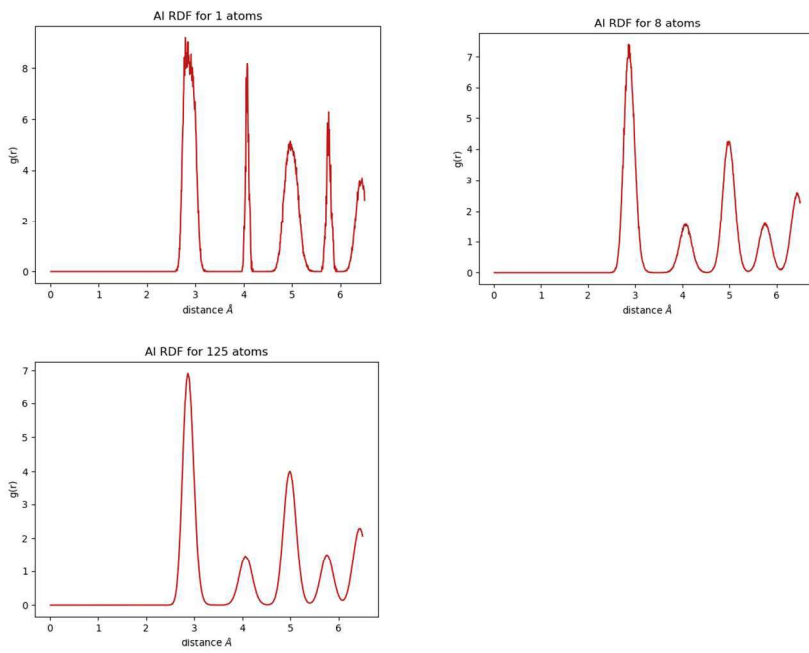Figure 5: Convergence of internal energy against timestep for Al and Cu

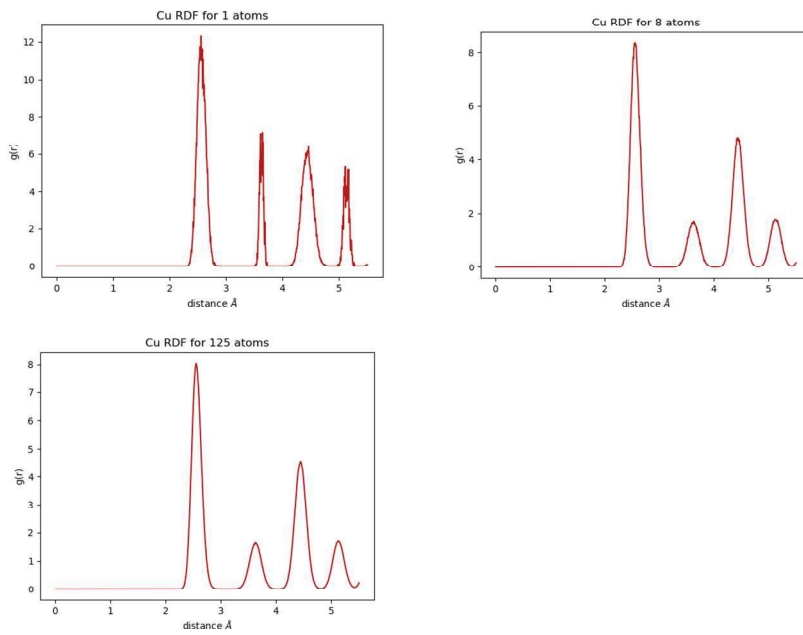Figure 6: Plots of RDF for Al for 1, 8 and 125 atoms

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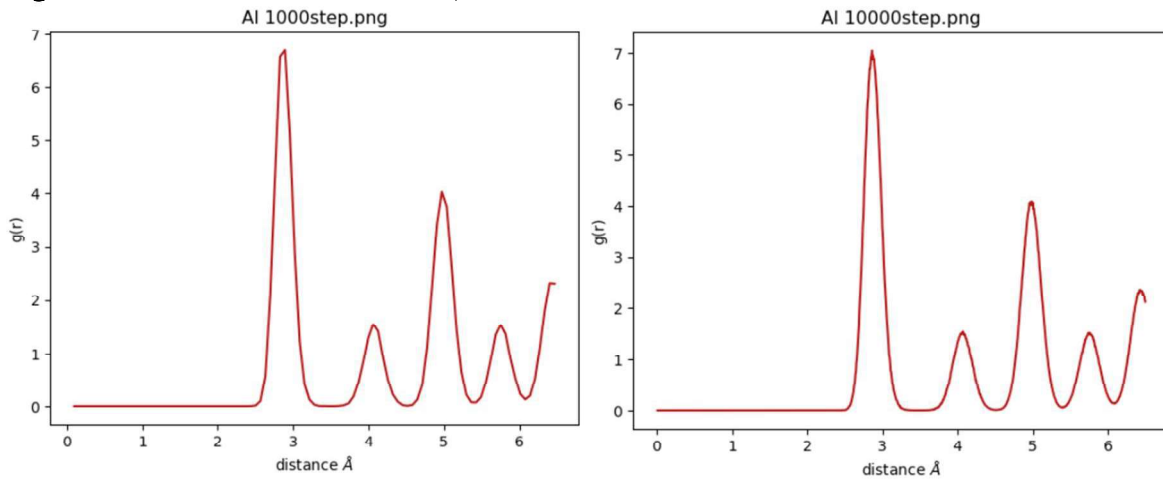Figure 7: Plots of RDF for Cu for 1, 8 and 125 atoms

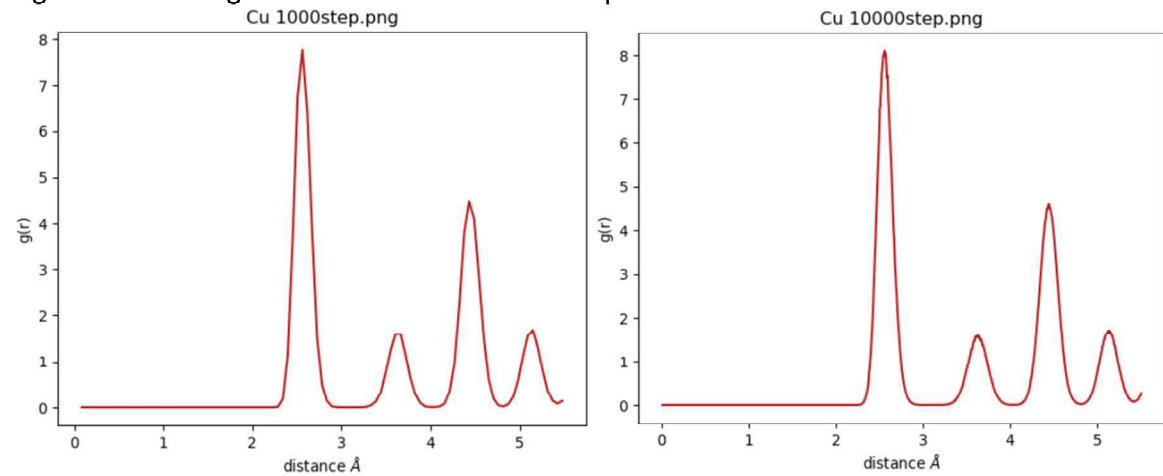Figure 8: Convergence of Al RDF with timestep

Figure 9: Convergence of Cu RDF with timestep

It was found that 512 atoms and 10,000 time steps is far more than sufficient for convergence. These parameters are used for the following results.

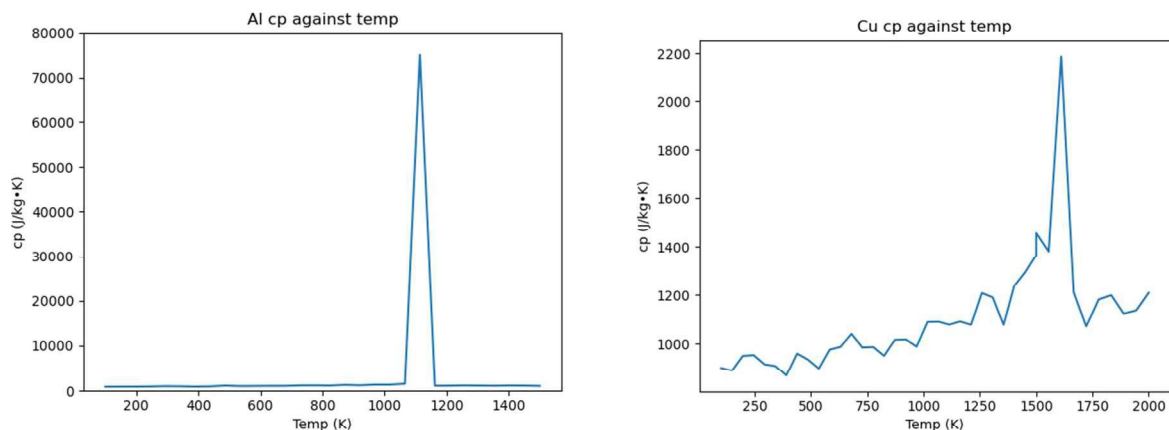**Cp, internal energy and RDF against temperature results**

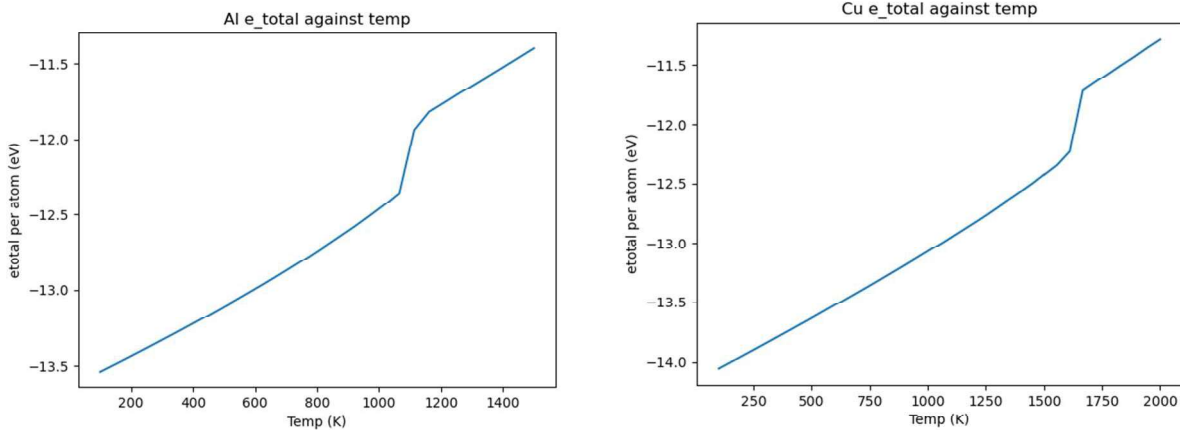Figure 10: Plots of cp against temperature for Al and Cu

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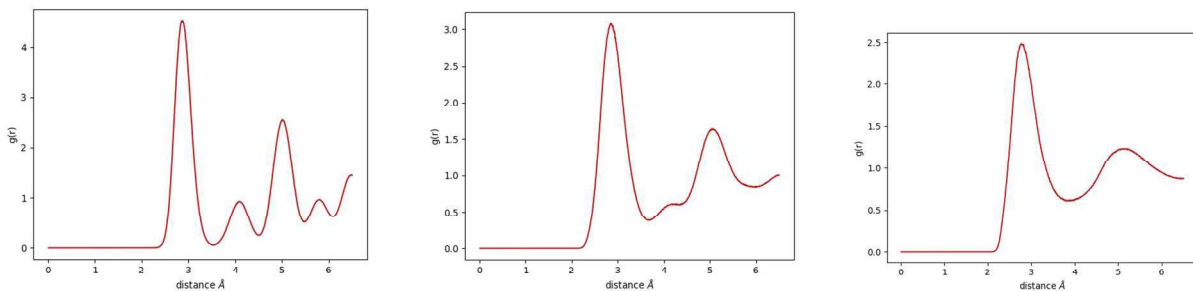Figure 11: Plots of internal energy against temperature for Al and Cu

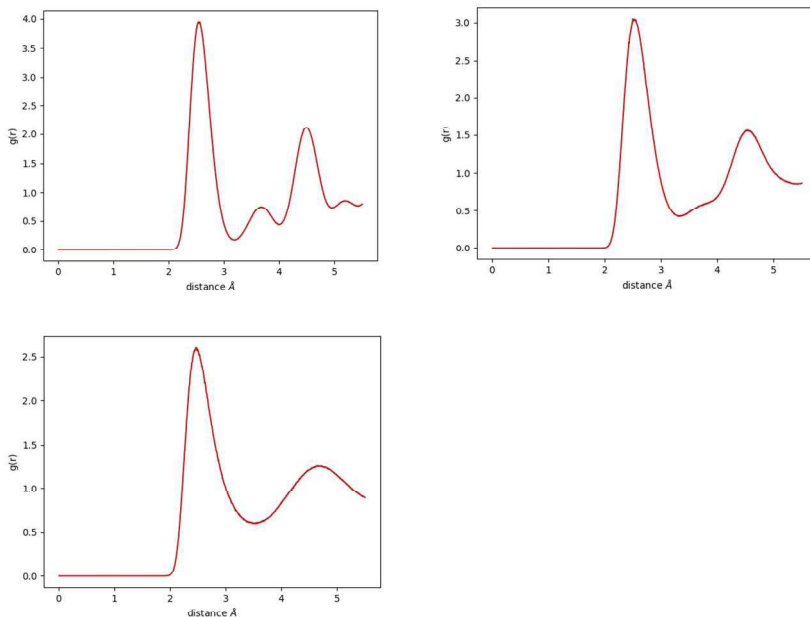Figure 12: Al RDF for 631, 1065 and 1114K

Figure 13: Cu RDF for 1065, 1555 and 1666K

From the graphs, by considering the start of the spike in cp and change in gradient in the internal energy plot as the melting point (m.p.), it can be determined that the m.p. of Al and Cu are around 1050 and 1550K. The experimental m.p. of Al and Cu are 933.3K 1358K resulting in percentage errors of 12.5% and 14.1%.

The cp, internal energy and radial distribution functions are calculated for 30 points between 100 to 1500K for Al and 40 points between 100 to 2000 for Cu.

Discussion

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The close to vertical behaviour of the internal energy at the melting temperatures are due to the energy being absorbed to overcome the metallic bonds of Al and Cu as the latent heat of fusion. It can be seen in the RDFs at different temperatures of Al and Cu when they start to deform and end up very similar when fully melted. This is because the RDFs simply reflect that of nearest neighbour behaviour that all liquids which are inherently amorphous possess.

Error analysis:
Any errors in the MD simulations would likely arise from not including all potentials or not using small enough timesteps.

Outlook section on how the project could be embedded in a broader multiscale modelling approach

The method calculates the melting point for materials by using the internal energy, specific heat and the radial distribution function. Information about the radial distribution function can be inputted into Gaussian which allows for the 3D viewing of the structure and understanding chemical mechanisms. The melting point of a material and phase is important to find the liquidus for CALPHAD. The specific heat is used to create CALPHAD databases and finite element simulations. In finite element simulations the temperature increase by absorption of energy affects the thermal expansion which determines the stresses of a simulated component. For alloys, the temperatures for the start and end of the spike in the cp and change in gradient of internal energy correspond to the solidus and liquidus lines in phase diagrams.

Summary and conclusion

Molecular dynamics has been demonstrated to be convergent and accurate in calculating the melting point, internal energy, specific heat and radial distribution function of single element lattices. It is also effective at determining the relative stabilities.