Helium interactions study in HCP Titanium through Molecular Dynamics simulation

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Abstract

In this work, the interactions of helium in a hexagonal close-packed titanium lattice are simulated. Density functional theory calculations are used to fit both Buckingham and Beck potentials to the helium-titanium interaction. Previous research has used a Lennard-Jones potential to good effect, but there are still physical aspects that this model cannot recover. This research recovers the experimentally observed helium clustering using the Beck potential, but fails to recover z-direction helium diffusion with either potential. In addition, the temperature dependence of helium clustering is found to be that the helium must start with energy between 850 K and 1200 K while the titanium lattice should be held at room temperature, 300 K.

Background

Helium diffusion in titanium is well-researched topic in computational physics. This process is important for a number of reasons. First, titanium can be used to store helium effectively. For instance, hydrogen and hydrogen isotopes are insoluble in certain types of titanium at room temperature [1]. Second, titanium has many applications in nuclear materials, and some nuclear processes result in a large gas build-up of helium by-products [2]. This makes it important to study how these gas build-ups can affect the titanium materials around them.

Experiment has demonstrated that helium accumulates in metals and forms small, highly pressurized bubbles [3]. These bubbles weaken material properties of the metal substrates, but their formation is not well understood [1]. This is what makes computational physics an important tool in the study of this bubbling effect.

It has been shown that in order to recover the helium bubbling effect in molecular dynamics simulations, the choice of He-Ti potential is very important. Previous attempts used a Born-Mayer potential and were unable to recover the bubbling effect [4]. Later, the He-Ti interaction was characterized by a Lennard-Jones function, and the bubbling effect was recovered successfully [1]. Finally, the diffusion investigation was taken one step further, and the diffusion of helium dimer and trimer were investigated. It was found that the different species of helium diffuse in different directions, and that for instance, helium dimer diffuses faster than single helium atoms [5].

Our group expands on previous research by constructing a custom He-Ti potential to attempt to recover the helium bubbling effect. Our justification is that it may be possible to model the effect in a way that agrees better with the physical picture. For instance, when the helium bubbles form within the titanium and generate such high pressures, the ideal gas picture of the interacting helium atoms is no longer valid, and constructing a new modeling potential could help reflect this.

Our method is to choose a typical potential such as a Buckingham potential and Beck Potential and then fit it to the form of an He-Ti interaction from first principle calculations. After obtaining this potential, we use LAMMPS to simulate the molecular dynamics and attempt to recover the helium bubbling.

Potentials

Ti-Ti

The titanium-titanium interaction that was chosen is that of the Finnis-Sinclair embedded atom model [6]. This potential is of the form shown below.

$$E_i = F_\alpha \left(\sum_{j \neq i} \rho_\beta(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij})$$

This form was chosen since it is widely used in molecular dynamics for metallic systems. To see how accurate the NIST data file was describing this potential, the titanium lattice was allowed to equilibrate from different lattice parameters. This equilibration process involved heating the lattice from 200K to 300K using the LAMMPS software and computing the energy and lattice parameters afterwards. The results of this thermal equilibration and the corresponding values from the literature are tabulated below, where the literature values are from Wood (1962) [7]. The agreement is quite close, which confirms that this titanium-titanium interaction potential is well-suited.

Data Set	Lattice Constant a (Å)	Ratio a/c (Å)
Equilibration Results	2.966	1.591
Wood (1962)	2.9511	1.5873

He-He

For the helium-helium interaction, the work of Aziz (1992) was used. The below plot shows (Fig.1) Aziz's semi-empirical data with the solid line, and the corresponding Lennard-Jones fit with the dashed line.
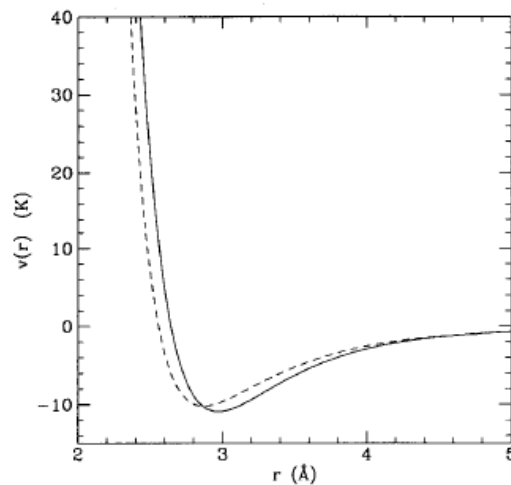

Fig 1. He-He potential. Solid line: Aziz potential and dash line: Lennard Jones

The coefficients for this Lennard-Jones fit are ε = 10.22 K and σ = 2.556 Å. The form of the Lennard-Jones used to model this helium-helium interaction is the form used below.

$$E = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \qquad r < r_c$$

He-Ti

For the helium-titanium interaction, density functional theory (DFT) was used to plot the energy as a function of distance. DFT calculation is carried out by VASP-a plane wave density functional code [8]. A cubic setup of 16ÅX16ÅX16Å size is used in which one O and one Ti atom is placed. Both these atoms are treated with projector augmented-wave (PAW) method with the PBE generalized gradient approximation [9]. In the calculation a helium and a titanium atom are placed at many different distances apart and calculate the energy between them at each of these distances. The resulting data was then able to be fitted to two different forms – Buckingham and Beck potentials. The resulting fits as well as the DFT calculation data is shown in the plot below. (Fig. 2)
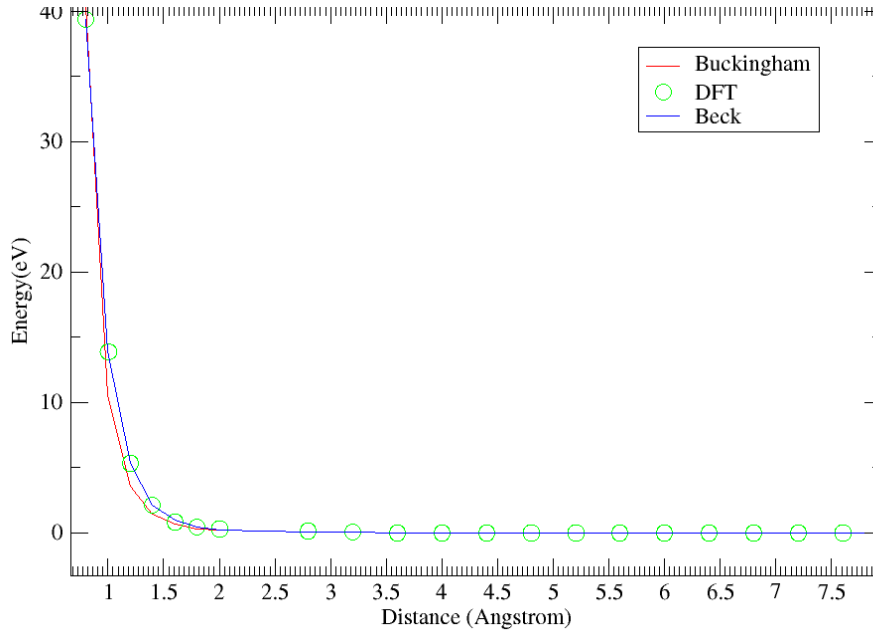

Fig 2: He-Ti potentials curve fitted to DFT data

As can be seen, both the Buckingham and the Beck potentials produce good fits with R^2 values roughly greater than 0.9.

Buckingham Potential

The Buckingham potential form is shown below.

$$E = Ae^{-r/\rho} - \frac{C}{r^6} \qquad r < r_c$$

The coefficients extracted from the Buckingham fitting function are tabulated below.

Coefficient	Value
A	197.93
ρ	0.0081135
C	-5.13237

Beck Potential

The Beck potential form is shown below.

$$E\left(r\right) = A\exp\left[-\alpha r - \beta r^6\right] - \frac{B}{\left(r^2 + a^2\right)^3}\left(1 + \frac{2.709 + 3a^2}{r^2 + a^2}\right)$$

The coefficients extracted from the Beck fitting function are tabulated below.

Coefficients	Value
A	-1.68955
B	-11.5121
a	0.681936
α	-3.55795
β	13.3602

Ensemble & Setup

For this simulation, LAMMPS software was used. The 1 time step corresponds to 1 femtosecond. The typical running time for a simulation was between 50,000 to 500,000 steps. The ensemble employed is canonical ensemble (NVT). The reason NVT was chosen over NPT, was that previous research suggested that the helium cluster effect is created from helium atoms displacing titanium atoms into interstitial spaces at constant volume [5].

In addition, typical runs used a 10x10x10 titanium lattice (4000 atoms) and 20 helium atoms with Periodic boundary condition in X, Y and Z direction. At first, helium atoms were placed randomly into the lattice, however the distances between the atoms in random placement could often be too high for anything to happen in the given simulation time. For this reason, the helium atoms were given specific placements roughly one lattice spacing apart from each other (3 Å).

For a standard run, the helium atoms were given an initial velocity corresponding to a higher temperature than what the titanium lattice was held at. This was done to give the helium atoms enough energy to displace titanium atoms before coming into a stable equilibrium state corresponding to system temperature. Typical starting energies for helium atoms was 600 K-1200 K, and the system temperature was varied between 300 K – 800 K. Nosé–Hoover thermostat is employed to fix the temperature.

Results

Z-Direction Diffusion

One of the objectives of these simulations was to recover helium diffusion in the z-direction through a titanium lattice [5]. For the majority of these attempts, the helium would simply vibrate around its starting location and never diffuse. One reason for this could be that since the diffusion process is extremely slow, it just was not observable in the length of these simulations. Another reason could be that the chosen potentials simply did not capture the diffusion process. In an attempt to observe any sort of diffusion, unphysical restraints were placed on the system. In the figure below, two helium atoms were held at an energy corresponding to a temperature of 2000 K. The titanium lattice

was held at 500 K, although this choice was arbitrary and room temperature of 300 K produced the same results. The Fig. 3 displays 500,000 time steps trajectory of 2 helium atom all being superimposed.
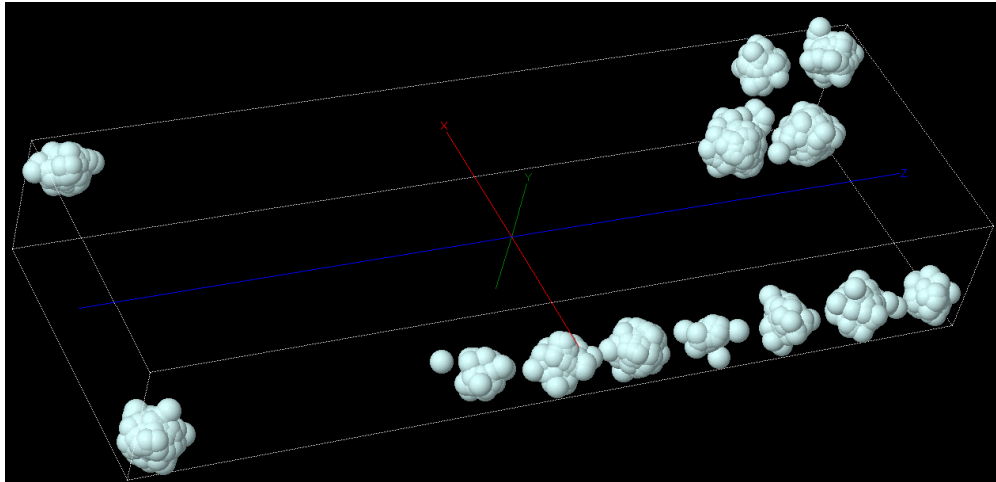

Fig 3: Superimposed two He atom trajectories for 2,50,000 time steps. Blue axis represents the z-axis

The effect that occurred is that the helium atoms would vibrate in place and then after some time they would make a jump in the z-direction. In the top right corner of the figure, there is a noticeable x-direction jump which probably stems from the unphysical restraint placed on the system. Also, this process does not look like diffusion, and the particles always move in the positive z-direction instead of the negative z-direction. For this reason, it is suspected that what is being observed is simply momentum causing the particle to jump in the z-direction. This suspicion is granted credibility since diffusion is a random walk and occurs when the system is in thermal equilibrium, which is not the case in this run.

Helium bubbling (clustering) Effect

The helium clustering effect was recovered on the timescales of these simulations when the helium atoms started out at lattice spacing distances apart. Note: these clusters were formed with the Beck potential only. These clusters formed quickly (9,000 time steps) and were stable throughout the rest of the simulation (2, 50,000 time steps). An example of this clustering effect is shown in the Fig. 4. (a) Starting configuration with 20 He atoms distributed in center b) Cluster formed after 9,700 steps
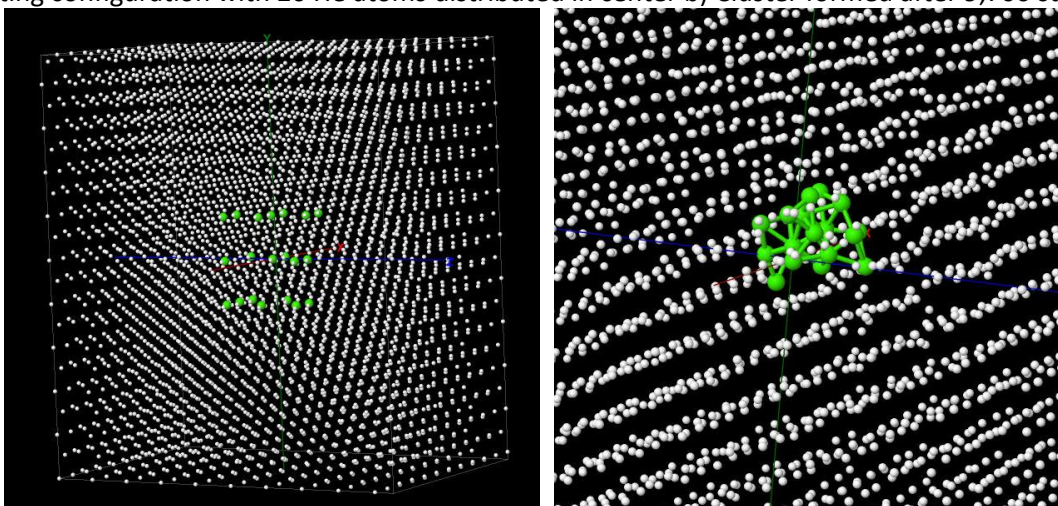

Fig 4: (a)Initial configuration of system (b) Configuration after cluster formation. White: Ti,Green:He

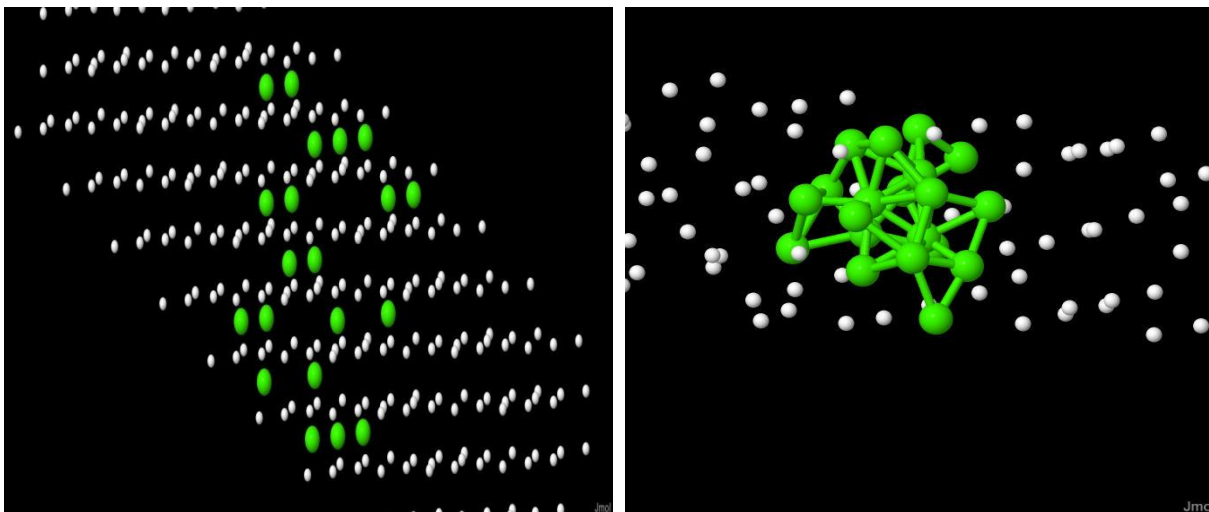In the figures below (Fig. 5), we see this same picture in a closer view.

Fig 5: Closer view of (a)Intial He atoms distribution (b) He Cluster White: Ti,Green:He

In the two figures below, we see this clustering effect without the titanium atoms obstructing the view. The bonds that are drawn are not physical bonds, but rather representations that the atoms are very close together. For instance, the starting distance between helium atoms was 3 Å and the final average distance after a nice cluster had formed was 2.05 Å.
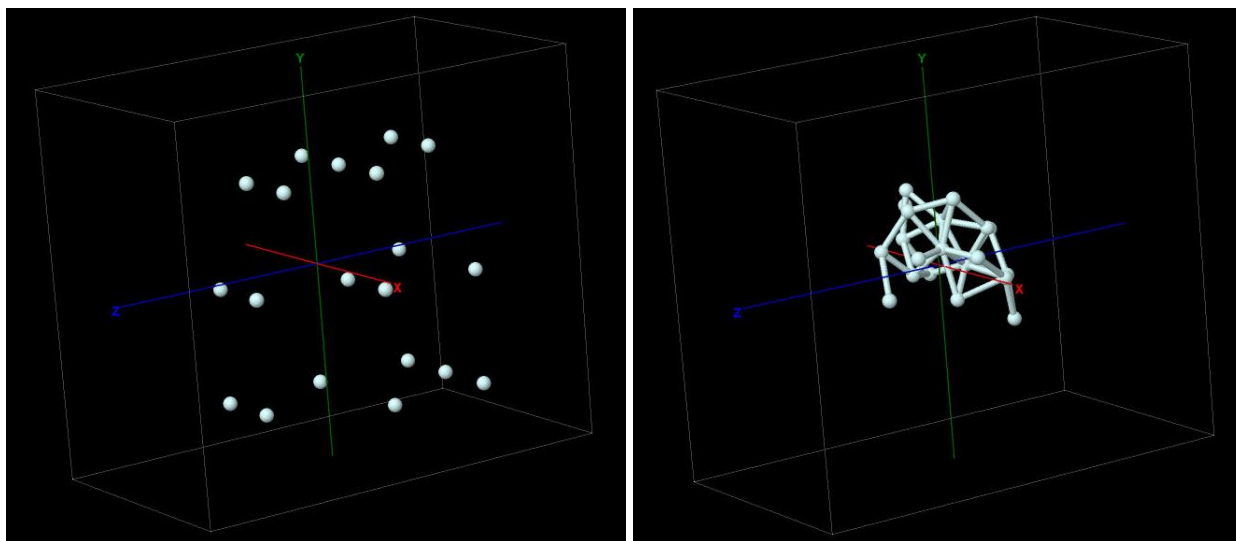

Fig 6: Ti atoms are hidden (a) Intial He arrangement in Ti Lattice (b) He atom cluster

Finally, to quantify this clustering effect, the radial distribution function was calculated for a helium cluster. As can be seen in the Fig. 7, there exists a peak at 2.05 Å. This corresponds to the interparticle spacing of the helium atoms that signifies that a cluster has formed.
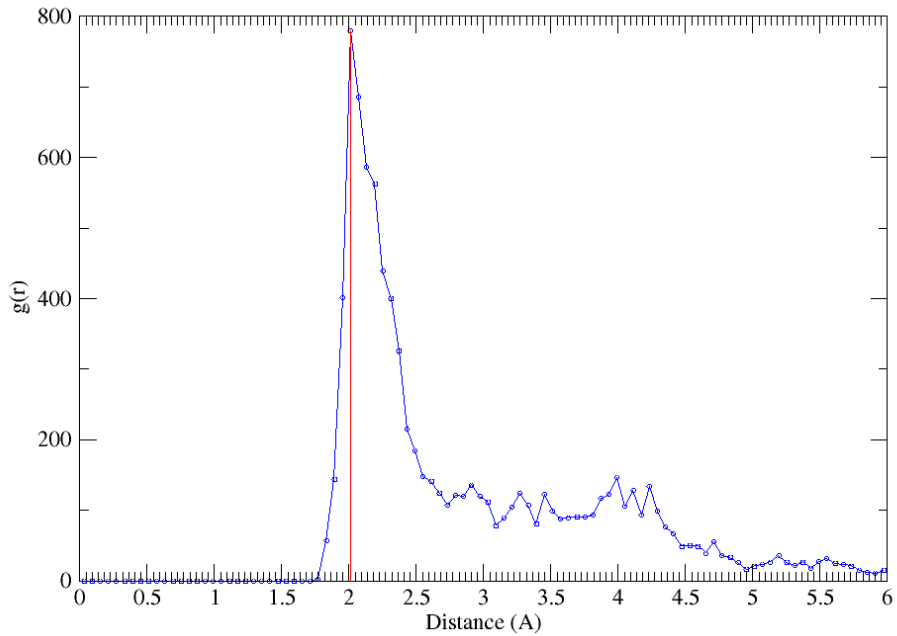
Fig. 7: Pair correlation function of He atoms in cluster configuration. Red line represents the cluster size

Similarly, since the helium particles were clustering in a titanium lattice at constant volume, this means the titanium atoms had to be forced into interstitial locations in the lattice. The high energy He atoms displaces the Ti atom from their lattice position into interstitial resulting into vacancy at Ti lattice. He atoms tends to agglomerate at these vacant site and forms the cluster. This mechanism of cluster formation is studied energetically by [10] and inferred that He forms vacancy-complex compound of He_nV type whose formation energy is negative making them the stable specie in system. The figures below illustrate the void (collection of vacancies) created by the helium atoms in Ti lattice. The fig. 8(a) is the before picture and the fig. 8(b) after the helium have clustered into the void. The void of titanium atoms is circled.
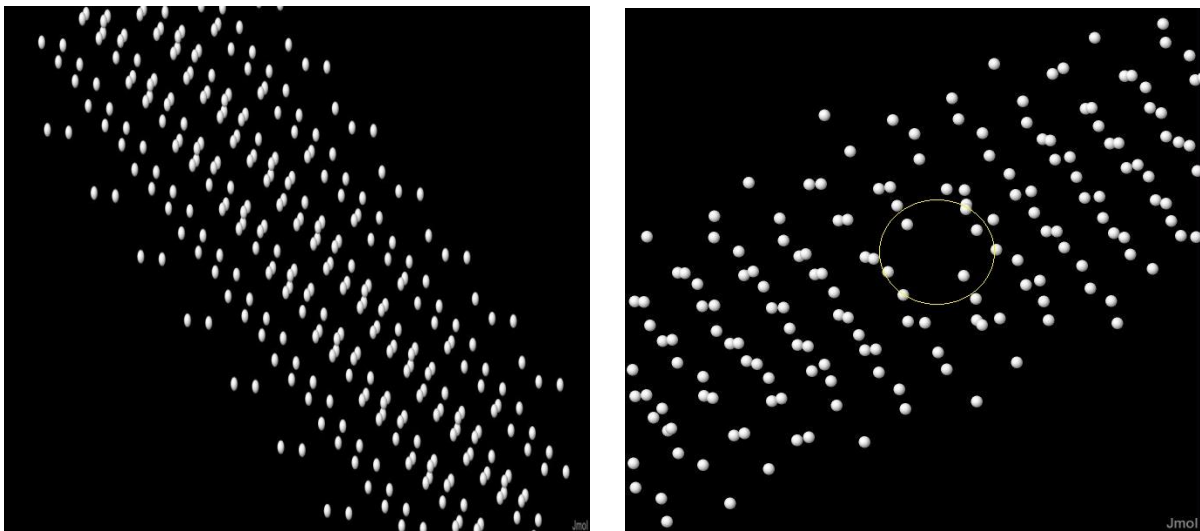

Fig. 8: He atoms are hidden (a)Perfect hcp lattice in initially (b)Void circled yellow in the lattice after cluster formation

The radial distribution for the titanium lattice is calculated before and after helium clustering to quantify these results. The plots are shown in the Fig. 9
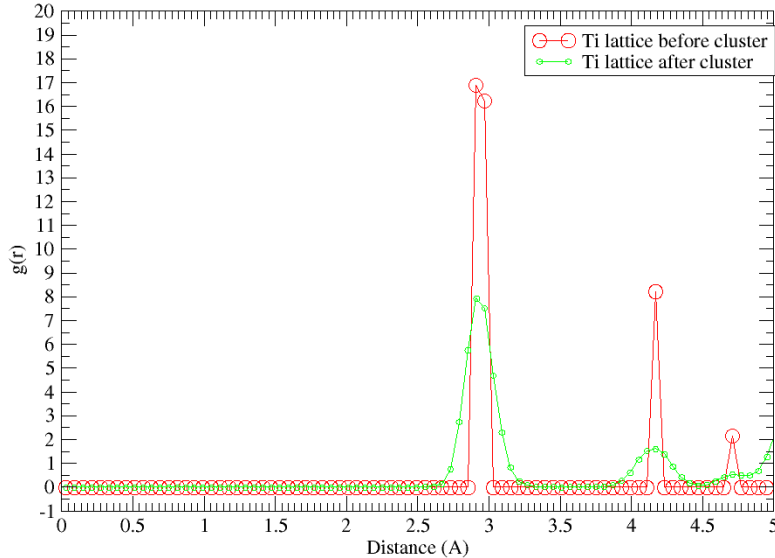

Fig. 9: Pair correlation function of Ti atoms in before cluster and after cluster configuration

Pair correlation function corresponds well to the hcp lattice. As expected (red line) three peaks are observed at distance a, $(2)^{1/2}$a and c which corresponds to first, second and third nearest distances in hcp respectively where a=2.96 Å and c=4.71 Å are hcp Ti lattice parameter. As can be seen, there is a significant drop in the pair-correlation function peaks before and after clustering which might hint the lowering of nearest neighbor due to void formation. In first principle study [reference] they attributed that

Temperature Dependence of Helium Clustering

Finally, the temperature dependence of helium clustering is examined in two ways. First, the helium atom temperature corresponding to their initial energy is varied while the system is kept at a constant 300 K. The results for various starting helium energies are shown in the Fig 10.
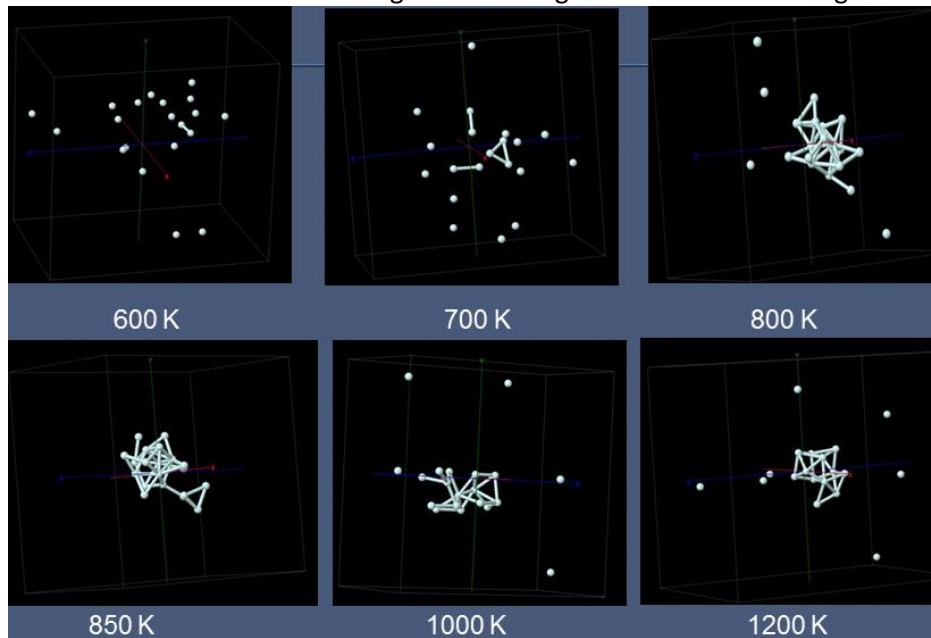

Fig. 10: Cluster formation tendency variation with initial He atoms energy corresponding to 600 K-1200 K

In the above figure, it is seen that the helium atoms require a higher starting energy in order for a cluster to form. The best cluster result is seen at initial helium energies corresponding to 850 K. The reason that no cluster forms for lower initial helium energies is most likely that the atoms do not have enough energy to displace the titanium atoms from their lattice locations.

As the temperature of the helium atoms increases further the cluster starts to split apart again. This could most likely be attributed to the helium having too much energy for the He-Ti interaction to make the helium atoms prefer to cluster.

The second method for examining the temperature dependence of helium clustering in a titanium lattice was to start the helium energies at an initial energy corresponding to 850 K while varying the temperature of the lattice between 300 K and 800 K. The results for these changes are illustrated in the figure below.

It can be seen that the cluster formation falls apart as the constant lattice temperature is increased from 300 K. The reasoning behind this is suspected to be that as the lattice temperature increases, the titanium atoms are given enough energy to re-enter their lattice locations and force the helium atoms back into the interstitial sites. At lattice temperatures comparable to the initial helium temperatures, it can be seen that virtually no clustering takes and the helium atoms actually separate farther from their initial configuration.
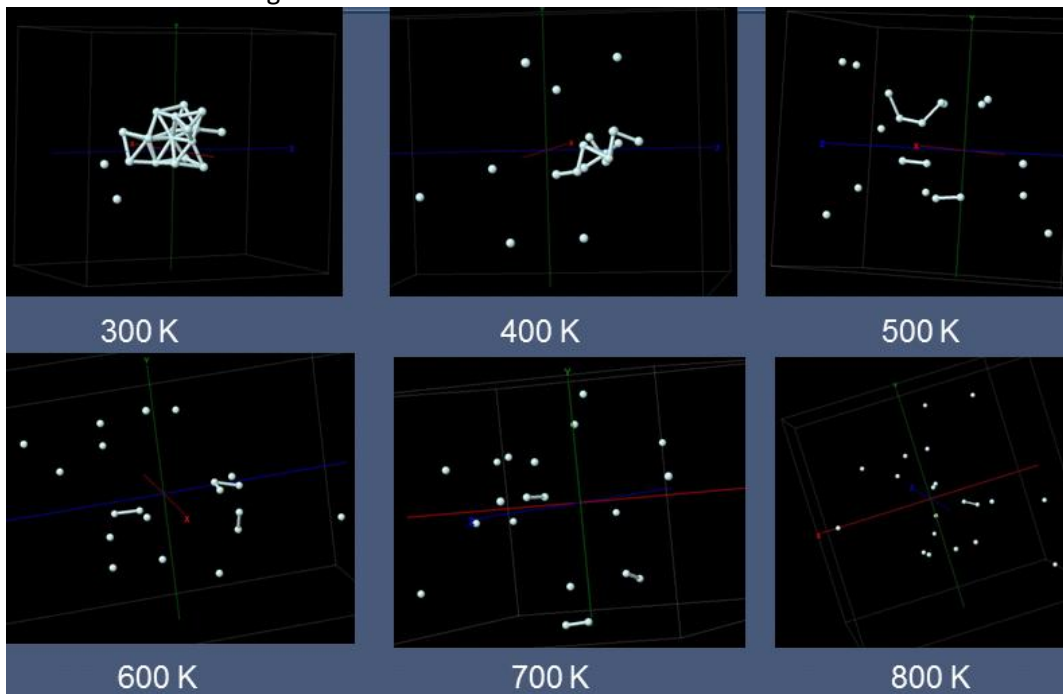

Fig. 11: Cluster formation tendency variation with system temperature from 300 K to 800 K

Buckingham Potential Results

All of the above results were using the Beck potential. The Buckingham potential was unsuccessful in producing any clustering. Recall that both the Beck and Buckingham potential fits to the density functional theory were extremely close. This gives credence to previous research stating that recovering the clustering effect is extremely sensitive to choice of potential [1]. This result could have also been predicted. This is because the Buckingham potential is a special case of the Born Mayer potential which was already unsuccessful in previous work [4].

Conclusion

In conclusion, this project aimed to simulate and study the interactions of helium inside of a typical hexagonal close-packed titanium lattice. The simulations aimed to recover two experimental observations of z-direction helium diffusion in the lattice, and helium clustering. To carry this out, density functional theory was used to find suitable fits for the Buckingham and Beck potentials to model the helium-titanium interactions. Out of these, only the Beck potential was successful in reproducing the cluster effect. Neither model successfully demonstrated z-direction helium diffusion. Finally, the temperature dependence of helium clustering was determined to be that helium must start with a sufficient amount of energy such as 850 K, but not too much higher than this, while the titanium lattice should be held at a lower temperature around 300 K.

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