Annealing HCP Crystal Grain Boundaries Using the Morse Potential

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(Dated: December 17, 2022)

Throughout this paper, crystal structures will be simulated using the Morse potential for three-dimensional particle interactions. Common crystal structures will be analyzed for varying values of the Morse potential. Also, the efficacy of annealing to heal grain boundary crystal defects will be considered. Specifically, two HCP lattices will be brought together with a grain boundary offset by 30 degrees. First, the crystal will be cooled to determine the ground state of the lattice. Then, the crystal will be annealed in an attempt to lower the ground state energy by removing crystal defects at the grain boundary. A annealing curve (for heating and cooling) was empirically determined which allowed for the grain boundary to be healed. With this heating curve, the crystal's defects were almost completely healed and the ground state potential was decreased by 1.1% relative to the crystal before the defects were healed. Additionally, the HCP lattice was converted to a FCC lattice as a result of the annealing process.

I. INTRODUCTION

In this paper, we explore the use of the Morse potential to simulate three-dimensional crystal structures and analyze varying values of the α parameter. We also examine the effects of annealing on healing grain boundary crystal defects between two HCP lattices.

A. Morse Potential

The Morse potential exhibits the feature of common interactions between particles found in nature. For example, it exhibits a hard-core radius that prevents particles from becoming close; however, it also has a global minimum for a finite radius. Particles are attracted together when they are at a distance and are repulsed when they are too close. As two particles get infinitely far apart, the slope of the potential is zero. This is displayed in FIG. 1. Additionally, for this paper, the distance to the well and the depth of the well are assumed to be equal to 1.

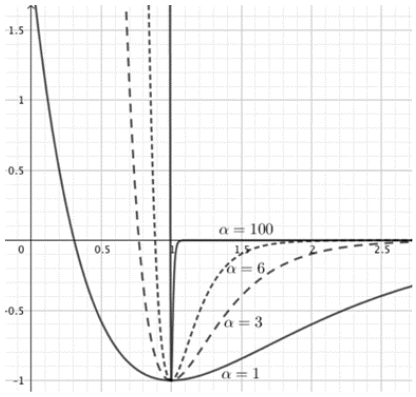

FIG. 1. The Morse potential for multiple α [1]

B. Common Crystal Lattices

There are a few crystal structures of interest regarding the Morse potential. First of all, the cubic lattice is the simplest and has particles at a uniform distance in three orthogonal directions. Second, the FCC (face-centered cubic) lattice is a cubic lattice with particles in the middle of all 6 faces. It is described with the three basis vectors seen above. The third is the BCC (body-centered cubic) lattice which has a cubic structure with a single particle in the middle of the cube; likewise, it can be fully characterized with the basis vectors seen above. Finally, the HCP (hexagonal close-packed) lattice can be seen as a triangularly tiled plane stacked on another triangularly tiled plane that is flipped.

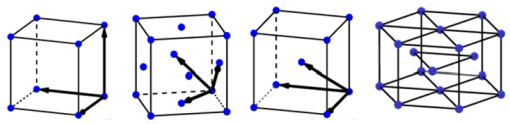

FIG. 2. Common Crystal Structures [1]

For the Morse potential in three spatial dimensions, the cubic potential is only a local minimum. For the other three crystal structures, the parameter α determines what the global minimum is. For small values of α, which correspond to wide potential wells, the BCC lattice is the global minimum ($\alpha < 3.05$). For a narrow intermediate range of α, the FCC lattice is the global minimum ($3.05 < \alpha < 3.55$). Lastly, for large values of α, the HCP lattice is the global minimum ($\alpha > 3.55$) [1].

Interestingly the FCC lattice and the HCP lattice have the same atomic packing factor of about 74% [2]. Their similarities don't stop there either. Every particle has the same number of neighbor particles 12; this is known as the coordination number [2].

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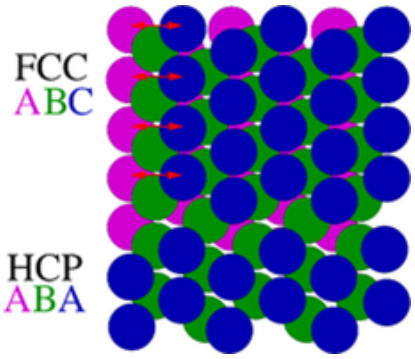

FIG. 3. FCC and HCP Stacking Fault [3]

C. Miller indices, Defects, and Annealing

Another interesting property of crystals is the shape of the edge of the lattice. Miller Indices are a system of notation commonly used to describe the planes or directions of atoms in a crystal lattice structure. They are three integers, which refer to the relative distances between atomic planes parallel to each other in the lattice. The indices can be used as an easy way of describing the orientation of a particular plane in a crystal structure without having to describe its exact position in terms of x, y, and z coordinates.

Miller indices are useful to show the similarity between the HCP and FCC lattices. If you slice an FCC lattice along its 111 plane. The surface will be the same as an HCP along its 100 plane. in FIG. 3, a 111 FCC lattice is joined to a 100 HCP lattice. This figure also shows the stacking pattern of FCC along its 111 plane is ABCABC whereas the HCP stacking pattern along its 100 plane is ABAB. Overall, the HCP and FCC lattices are very similar and only deviate by a stacking fault.

There is another interesting type of crystal defect called a grain boundary. This is where two of the same crystal structures are misaligned as seen in FIG. 4.

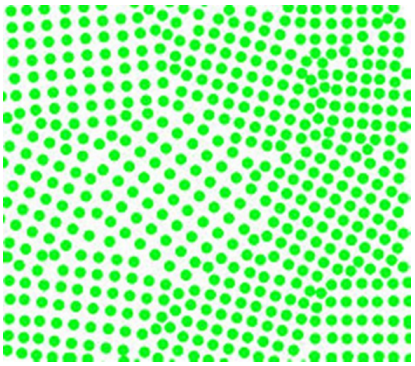

FIG. 4. Grain Boundary [4]

Annealing is a method in which a crystal is heated up to allow particles to move around more freely. The crystal is slowly cooled as a function of time, and as a result, particles tend to move to lower energy levels. The randomness of the particle movement allows the system energy to get out of local minimums and the slow cooling makes higher energy states less and less probable. This can lead to a decent approximation of the global minimum.

II. METHODS

All of the atomic interactions were modeled with the Morse potential. However, the well-studied Lennard-Jones potential was also trialed in some experiments. Despite the fact that it is comprised of less intense operations, it yielded no noticeable difference in the computation speed of the Python code. This could have been due to Python's inability to optimize low-level operations or due to x86 architecture offering speed improvements for the exponential operator, speeding up the Morse potential calculations.

In order to simulate the particle positions while conserving quantities such as energy, symplectic algorithms were used such as the Cromer algorithm and the velocity-verlet algorithm. This allowed the simulation to proceed with almost a steady total energy throughout the entire simulation.

Finally, in order to account for the fact that the simulation must be finite, periodic boundary conditions were used. This boundary was fairly easy to implement in the simulation by ensuring that all distances in the simulation were bounded with the modulo operator.

In order to generate the lattices, two methods were used. The simple method is to generate a cubic lattice and then multiply the coordinates by a linear transformation. The transformation was chosen such that the cubic lattice basis vectors were mapped onto the basis vectors for the desired lattice. However, this yields a morphed crystal that does not have a cubic shape. For the HCP lattice a cubic shape was generated by shifting the rows and columns of a cubic array into the positions of a HCP lattice.

After lattices could be generated. They needed to be brought within proximity of one another to create a grain boundary. This was accomplished by giving a small and opposite velocity to each of the two crystals.

Once a grain boundary was created, the resulting crystal could be annealed. In order to anneal the lattices, at each time step or iteration, the velocity of all particles was multiplied by $1+\epsilon$ assuming $|\epsilon| << 1$. If this sum is slightly less than 1, then the system will slowly cool over time similar to how an actual crystal is cooled. Likewise, in order to heat a crystal, the velocities can be multiplied by a constant slightly greater than 1, such as 1.001.

All of the code and the rest of the details used to generate the data used in this paper can be found at `https://github.com/RyanVaughan/CrystalAnnealing`.

III. RESULTS

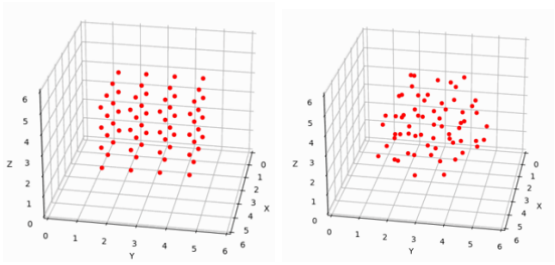

FIG. 5. Cubic lattice initial conditions and after a short simulation time

Since the cubic lattice is a local minimum, it tends to fall apart quite easily as shown in FIG. 5. It also has a surprising amount of energy in the structure because when it fell apart, it seemed to be in the liquid form.

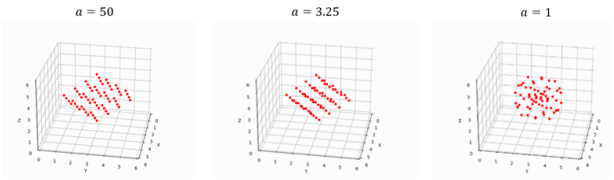

FIG. 6. FCC Lattice For multiple α

In FIG, 6, the FCC lattice is shown for three values of α. As the value of α changed, the distance between atoms in the ground state changed. The distance between atoms for high values of α closely approximated 1; however, for $\alpha = 3.25$, the ground state distance was about 0.94. This optimal distance kept decreasing until the crystal became unstable and melted for small values of α, such as $\alpha = 1$. As a result, larger values ofα were easier to work with and therefore the FCC and HCP lattice will be focused on. From here on out, $\alpha = 7$ unless otherwise stated throughout this paper.

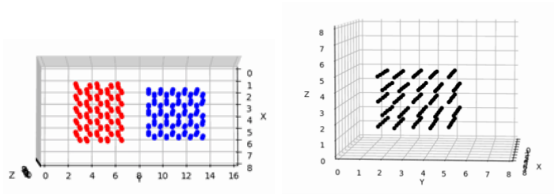

FIG. 7. HCP Lattice from different directions

The HCP lattice, as seen in FIG. 7 can be distinguished by the apparent hexagons from the z-dimension view. A side view of the HCP lattice can be seen as well. Notably, if the two planes shifted as shown in FIG. 8, the resulting lattice would be an FCC lattice.

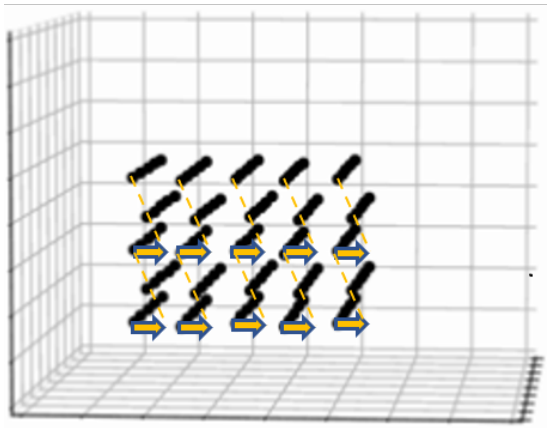

FIG. 8. HCP lattice with yellow arrows showing transformation to an FCC lattice

Now we will look at what will happen when we collide two HCP lattices with different edges. As seen in FIG. 7, the red and blue lattices are the same but rotated by 30 degrees about the z axis. We will analyze what happens when crystals in this orientation are brought close together.

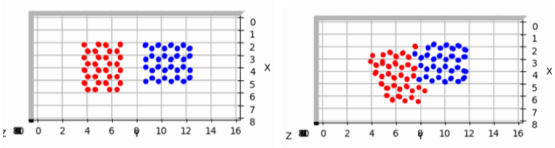

FIG. 9. Small HCP Crystal Boundary Healing

A small lattice with a grain boundary of 30 degrees immediately healed. This occurred because it was able rotate due to its small size. It kept the same grain direction and annealing was not necessary to get a single grain crystal.

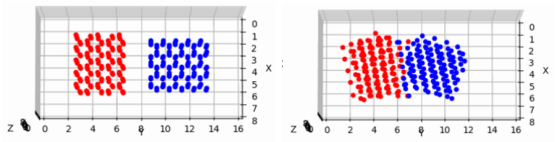

FIG. 10. Large HCP Crystal Boundary Healing

Next, a larger lattice was collided to see if it would have any dislocations. You can see that the grain direction changes once the crystals are brought together. However, there are also a concentration of defects near the grain boundary.

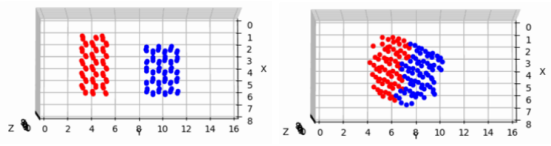

FIG. 11. Intermediate HCP Crystal Boundary Healing

Due to high simulation time of the previous lattice consisting of 250 particles (62250 interactions), the lattice depth was decreased so that there were only 150 particles (22350 interactions) as seen in FIG. 11. In a similar fashion, the crystal attempts to heal the boundary and ends up switching crystal orientation. However, there are still defects in the result.

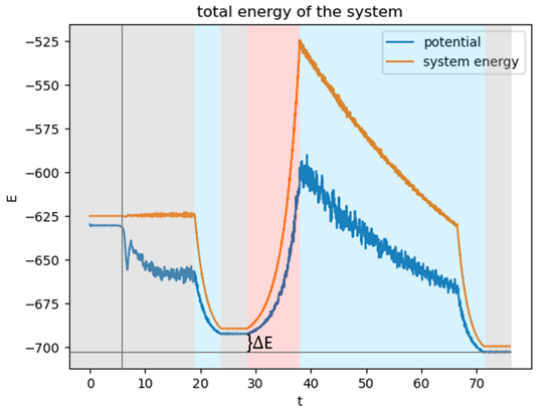

FIG. 12. Simulated Annealing Energy Curves

In order to heal these defects, the conglomerate crystal was annealed. As seen in FIG. 12, the two crystals are brought together at about $t = 7$. After which, the potential of the system decreased and therefore the kinetic energy of the particles increased. After the potential settled, the system energy was decreased to find the current potential ground state of the crystal. This can be seen as the first region in blue. Next in order to anneal the crystal, the crystal was heated up to an energy at which particles would move around significantly but not lose their overall shape. This energy level was determined empirically. After very slowly cooling the crystal, statistically, the defects tended to get healed. After a final quick cooling after the particles stopped moving positions, the new ground state was found and it was lower than the ground state prior to the annealing process. The difference in energy is denoted by ΔE. For this annealing process, $\Delta E = 7.5$. This is about 1.1% of the overall energy and gives a per particle energy difference of 0.05 energy units.

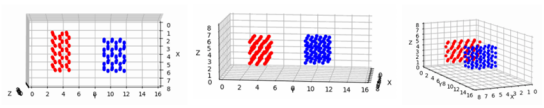

FIG. 13. Initial Conditions

FIG. 13 shows the crystal structures before the collision. These are regular HCP lattices.

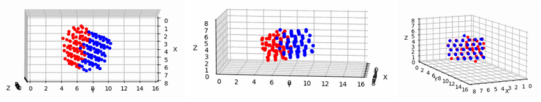

FIG. 14. After First Cooling

The result after the first cooling can be seen in FIG. 14. The crystal is still HCP as can be distinctly seen from the third view. The crystal direction is different from both of the seed directions, however. Some defects can be distinctly seen near the junction from the second view.

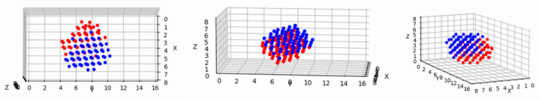

FIG. 15. After Annealing

After the annealing, the crystal structure changed as seen in FIG. 15. The crystal changed from HCP to FCC. There are only a few very small defects in the result.

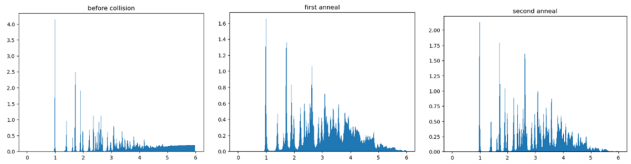

FIG. 16. Radial Distribution Functions

The radial distribution function of the three states are seen in FIG. 16. All three graphs have similar peaks due to the similar packing and radial symmetries of the HCP and FCC packing structures. However, before the collision, there are many particles that have a radial distance between 4-6 since the two crystals are far apart. After the first cooling, there is more noise in the distribution, the spikes are wider due to some of the defecting particles tweaking the lattice dimensions. However, after the annealing process was completed, the sharp peaks were regained due to the very regular crystal structure.

IV. CONCLUSION

Regarding the stability of crystal structures, the cubic lattice was shown to be only marginally stable. The FCC

and HCP lattices were shown to be stable - especially for large values of α. Overall, the annealing process was demonstrated to be effective for healing a grain boundary between two HCP lattices yielding a ground state energy that was 1.1% lower than that prior to annealing.

Interestingly, the crystal structure after annealing also converted from an HCP to a FCC lattice. The HCP structure is supposed to be the global minimum for $\alpha = 7$, but the simulated annealing process yielded a FCC lattice. This could be due to not enough simulation time given in order to find the ground state. The python code took a considerable amount of time to simulate over 100 particles for a sufficient time to allow particles to move and I believe more time should be allowed for annealing in subsequent studies.

This study is important in order to understand how the annealing process works and also to test the Morse potential against real-life phenomena such as annealing. The simple Morse potential is able to simulate such phenomena along with the aid of symplectic algorithms.

V. ACKNOWLEDGEMENTS

I would like to acknowledge Dr. Borunda for his insights and guidance with regards to this research project.

VI. APPENDIX - ANNEALING FAILURES

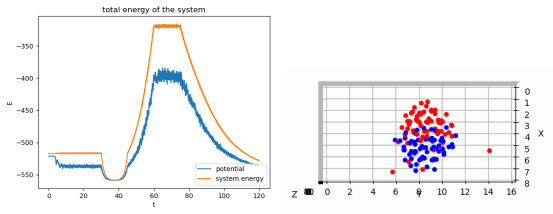

FIG. 17. Failed Annealing Attempt

As seen in FIG. 17, if the crystal structure breaks apart due to too much heating, it will be very difficult to get a seed crystal going and get back to find the global minimum. The annealing process ended up increasing the ground state energy. Many trials had to be taken in order to determine the right amount of heating that would be able to change the crystal structure but not too much so that the crystal completely melted.

[1] L. Bétermin, *Minimizing lattice structures for Morse potential energy in two and three dimensions* (2019).
[2] Brandon, *What is the Difference Between FCC and HCP?* (2022).
[3] G. Ziegenhain, *Comparison of fcc and hcp lattices* (2022).
[4] E. Pleshakov, *Micrograph of a polycrystalline metal* (2022).
[5] P. Segonne, *Animating a 3D scatterplot with Matplotlib* (2022).