Mechanical Engineering and Materials Science
Independent Study

Mechanical Engineering & Materials Science

12-20-2017

Metallic Glass Composites-Understanding Nucleation and Growth

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Introduction

When a metallic liquid is quenched, it typically forms crystalline phase. However, some metallic alloys when quenched rapidly bypass nucleation and growth and form amorphous phase. These amorphous phases, popularly referred as metallic glasses exhibit properties complimentary to their crystalline counterparts such as thermoplastic forming, higher corrosion resistance, higher strength. Although nucleation and growth is essential for solidification in metals, their atomic origin is not well understood. In this report, we have studied structural evolution of liquid in $Zr_{20}Al_{20}Ni_{60}$ metallic alloy as it cools down using molecular dynamics simulations.

Overview

Five-fold local symmetry(FFLS) is a type of local symmetry that is widely observed in nature from cross section of an apple to architectures [1]. Due to its incompatibility with long range order of crystalline symmetry, it has been shown that it is the structural parameter that differentiate crystalline and liquids/glass. It has also been predicted that this local symmetry could be a general parameter in understanding metallic glass and liquid [2].
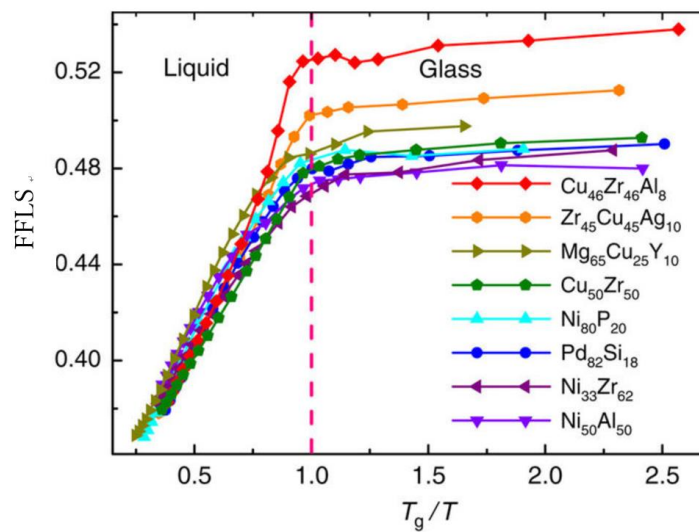

Figure 1. Typical FFLS of metallic glass [2]

In metallic glass-forming liquids, FFLS evolve with temperature change. Figure 1 shows typical behavior of FFLS in metallic glasses. As the temperature approaches the transition temperature (T_g), FFLS increases and remains high after the transition into metallic glass. In the case of crystal, FFLS rapidly drops after the transition into crystal. The FFLS for composite generally fall in the middle of these extremes after the transition.

Voronoi index is another useful parameter to examine local structures. It is constructed by bisecting connecting lines of an atom and its nearest neighbors with plains, which results in various type of

polyhedrons (2). Type i of a polyhedron is denoted by Voronoi index $<n_i^3, n_i^4, n_i^5, n_i^6>$ where n_i^k represents number of k-edged polygon in the polyhedron (3). Naturally, some indexes are associated with structure of crystal and liquids. For example, type <0,6,0,8> are strictly seen in BCC crystal and <0,3,6,4> is associated with FCC like structure. It follows that such polyhedron type is temperature dependent (3). Figure 2 shows typical formation of atoms for <0,3,6,4> and <0,6,0,8> polyhedron.
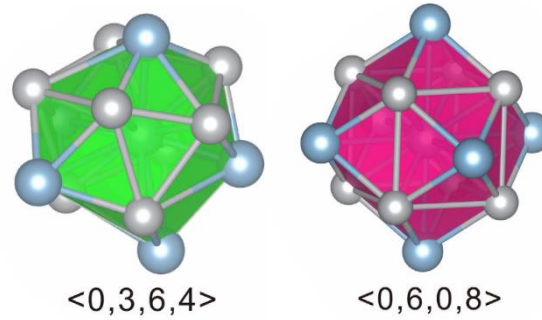
Figure 2. Type <0,3,6,4> and <0,6,0,8> polyhedron (4)

In a mathematical form, average FFLS in a polyhedron of type i can be expressed as

$$Average\ FFLS = \sum_i \frac{n_i^5}{\sum_{k=3,4,5,6} n_i^k} \times P_i$$

where P_i is fraction of polyhedron type i in the liquid (3).

While these FFLS and Voronoi analysis gives overall insight on nucleation and growth in metallic grass, they have not been applied to individual crystal and its nearest neighbors. In this independent study as a continuing work from my summer internship 2017, we have developed sets of computer programs that enables us to conduct similar analysis for each growing crystal and its nearest neighbors to better understand the process of nucleation and growth at atomic level.

Method

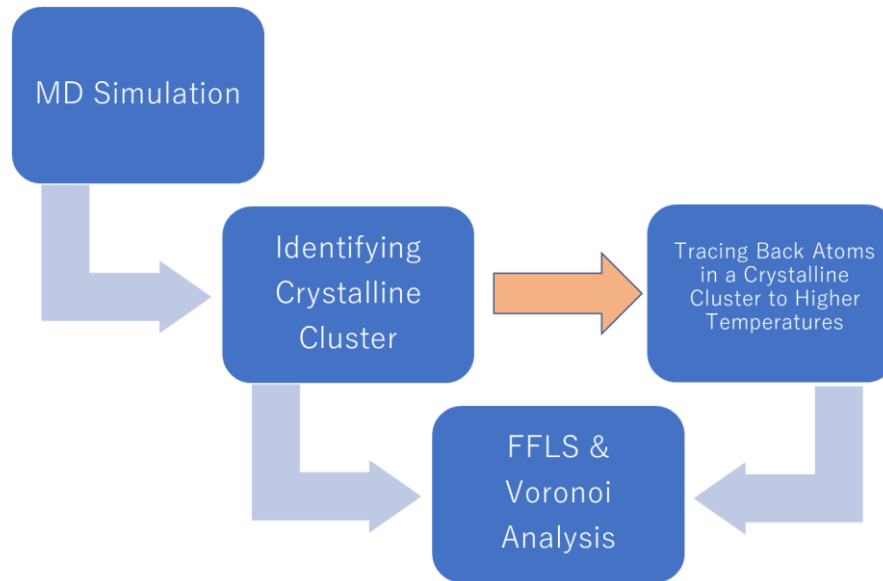Major parts of computer programs that we developed are briefly described in the Figure 3.

Figure 3. Overview of our program

- We use a glass-crystalline composite, $Zr_{20}Al_{20}Ni_{60}$ in our study. It solidifies around ~1000K for the quench rate used in our simulation. My program takes results of Molecular Dynamics (MD) simulations of $Zr_{20}Al_{20}Ni_{60}$ as input for each temperature, which contains information such as locations of atoms and their structural types. Structure types for each atom are obtained from Ovito which uses common neighbor analysis technique to identify the structure types (5).

- It identifies what we define as a "crystalline nucleus". It is a cluster that consists of atoms which are sitting on BCC crystal lattice as a core and neighboring non-BCC atoms. We set the minimum number of atoms in the crystalline cluster as 50 to identify nuclei. We defined cutoff distance for identifying nearest neighbors based on their radial distribution function. Cutoff distance used is 3.5 Å.

- It applies the five-fold local symmetry and Voronoi index analysis for each crystalline clusters as well as atoms in matrix that are not in any crystalline clusters. It partially uses preexisting algorithms from OVITO with some major modifications. This analysis is made for every temperature around the transition temperature.

- While we now able to investigate such parameter for each growing crystalline clusters, we also want to obtain the same parameter for atoms that eventually forms a crystalline cluster. For this purpose, final part of our program memorizes atoms of nuclei at transition temperature and traces them to higher temperature so that we can observe structural evolution of atoms involved in crystallization.

Furthermore, we applied above program to small and large MD system. As Figure 4 shows, MD simulation contains roughly 35,000 atoms and 1000,000 atoms for small and large system respectively. We start with small system to make sure our program works. We then try to analyze larger system of about 1000,000 atoms and compare it with findings from small system.
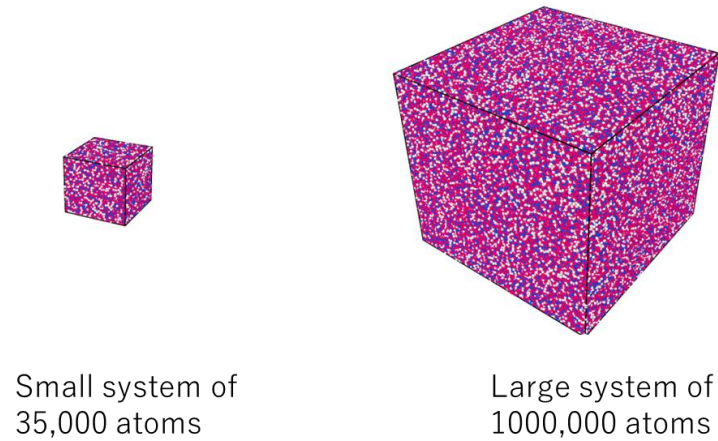

Small system of 35,000 atoms

Large system of 1000,000 atoms

Figure 4. Comparison of small and large system.

Al, Ni, Zr are colored blue, pink and white respectively.

Results

In figure 5, we show graphical results of our algorithm that identify the crystalline cluster made of BCC atoms and neighboring non-BCC atoms for small system of 35,000 atoms. We used OVITO to identify BCC atoms (5). As expected, several cluster started to grow as temperature decreases and eventually forms a dominant crystalline cluster.
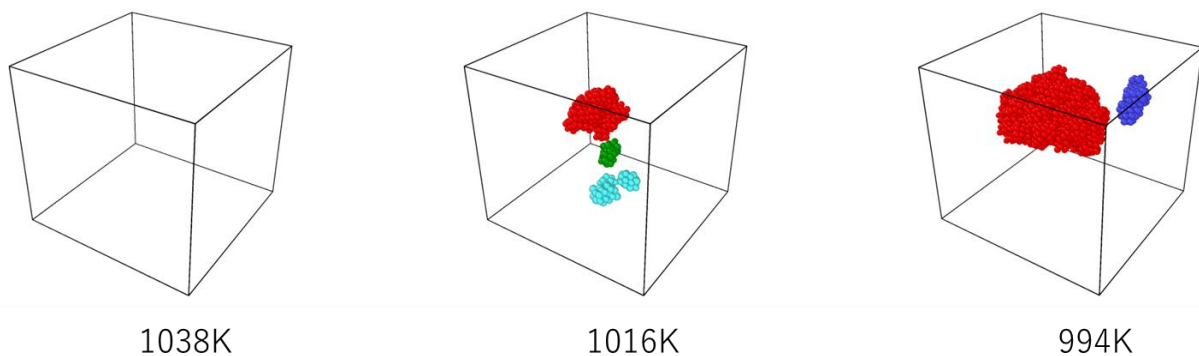

1038K

1016K

994K

Figure 5. Growing crystalline clusters in $Zr_{20}Al_{20}Ni_{60}$ in the small system.

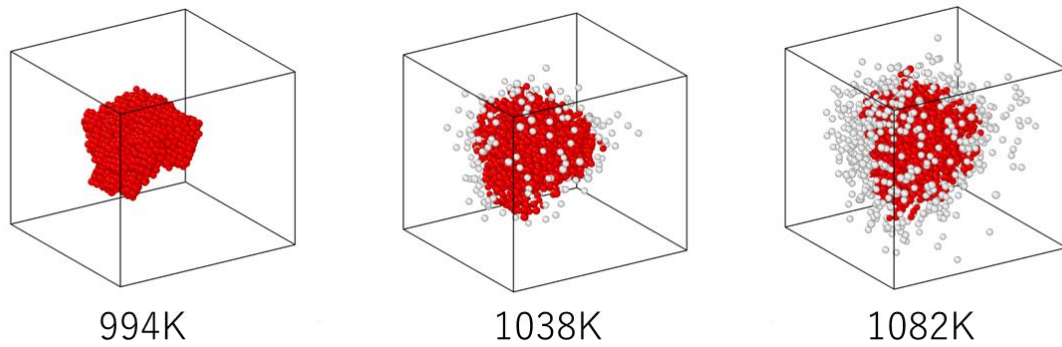**Each crystalline cluster is colored differently.**

Figure 6. Atoms of the nucleus traced from temperature 994K to higher temperature. Red color indicates atoms occupying BCC lattice. White color indicates atoms, which do not occupy BCC type lattice

Figure 6 shows atoms of nucleus at 994K traced back to higher temperatures. We do not include white-colored atoms in our analysis, that are too far away from other traced atoms.

Figure 7 shows the FFLS for all atoms in the small system. We confirmed quick drop in FFLS at the transition temperature 994K. We then apply the same analysis for each cluster using our program. We especially focus on a crystalline cluster that grows quickly and become dominant cluster at lower temperature, which is shown in Figure 6. We can see that low FFLS of crystalline cluster A shows signature of crystalline below the transition temperature. Furthermore, it remains low compared to overall FFLS even around transition temperature, which indicates the early transition for crystalline cluster A. Similarly, we obtain FFLS of matrix whose atoms do not form any cluster. In contrast to crystalline cluster A, the FFLS of matrix remains high even after the transition and clearly exhibits the signature for glass.

At temperature higher than 1016K, there are no crystalline clusters thus we cannot directly observe the symmetry in the clusters. However, as mentioned in the method section, we developed a program that trace the atoms in a cluster at the transition temperature, 994K to the higher temperature. In Figure 7, we show FFLS symmetry for the traced atoms at higher temperature. According to this, the atoms, which eventually form the cluster, again indicates early transition for crystalline cluster A, compared to overall transition.
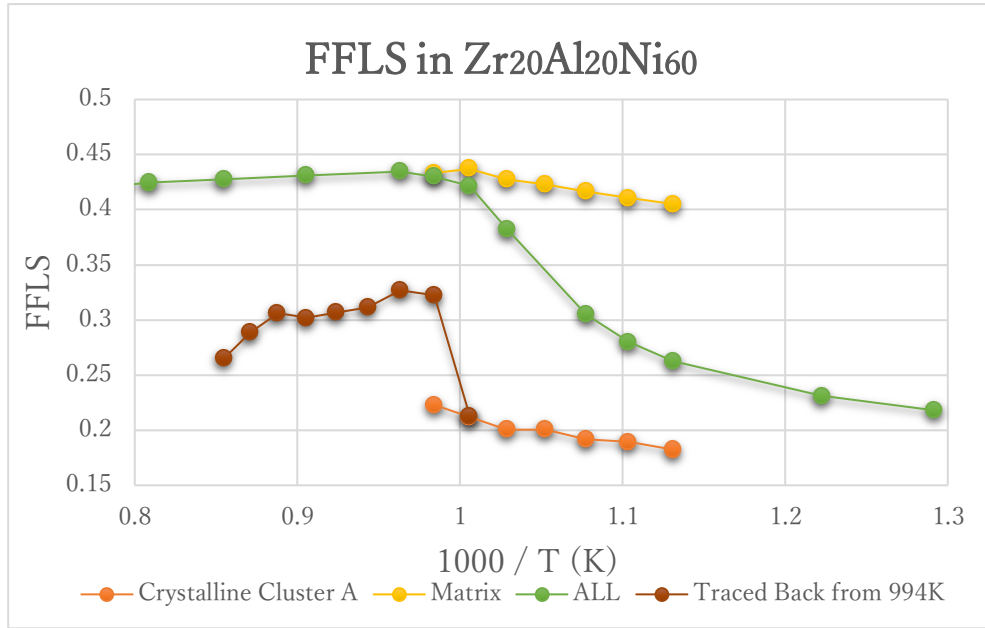
Figure 7. FFLS in Zr20Al20Ni60 in the small system

In Figure 8, we show the change in fraction of Voronoi index for all atoms around transition temperature. The most popular Voronoi index is dominant index <0,3,6,4> and decreases as temperature decreases. However, there is no dramatic change in this dominance, so this may suggests <0,3,6,4> plays important role during this transition.
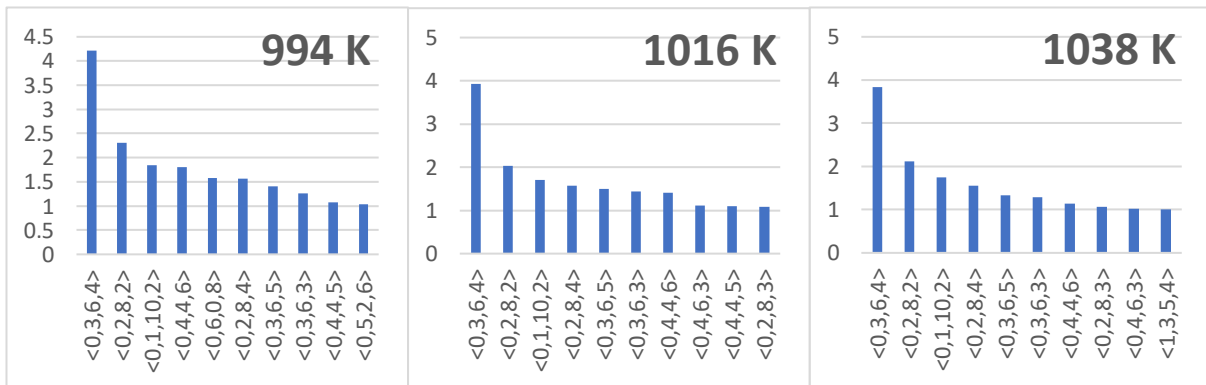

Figure 8. Voronoi analysis for all atoms in the small system

We also investigate the fraction of Voronoi index for crystalline cluster A as shown in Figure 9. We see the dominant index is <0,6,0,8>, which is associated with the BCC crystalline structure. Moreover, the <0,6,0,8> starts to be appear at 1016K before transition temperature and rapidly increase around the transition temperature.
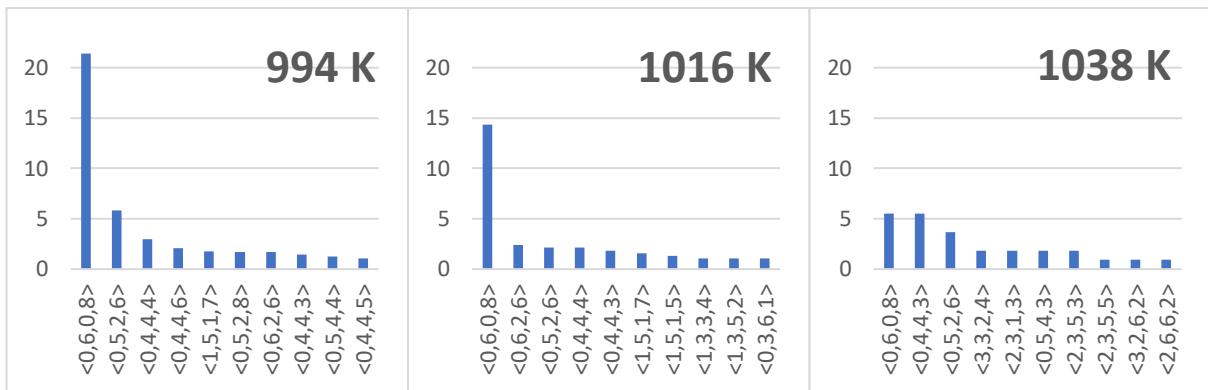
Figure 9. Voronoi analysis for Crystalline Cluster A in the small system

The same analysis is applied to traced atoms that are in the cluster 1 at 994K as in Figure 10. The dominance of <0,6,0,8> quickly disappeared even at 1016K , which indicates traced atoms do not show signature long before the transition.
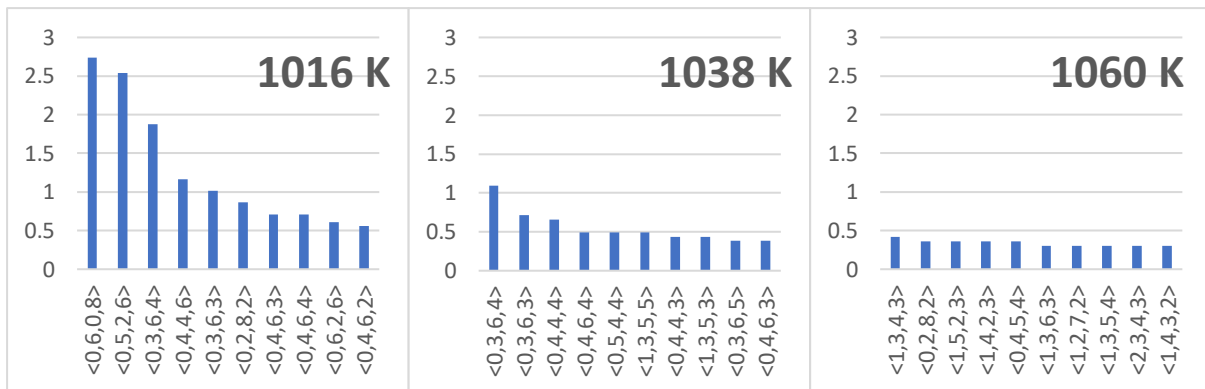

Figure 10. Voronoi analysis for traced atoms in the small system

Although we successfully develop programs and analyze its results for our small system, we need to scale up the system to be more confident about our observations. Since we have periodic boundary conditions simulation box, crystalline clusters in small box, quickly merges together, which might have affected out results. In larger system, crystalline clusters grow independently. This also enables us to make comparative analysis for fast-growing and slow-growing crystalline cluster in the future study.

For best performance, we run our program for larger system of 1000,000 atoms on Comet, which is dedicated cluster in super computer platform, XSEDE. However, we quickly learned our program needs some modifications to finish our analysis in allocated time. This is especially the case at lower temperature where there is large amount of crystal atoms. As of this moment, we are able to complete our analysis until 994K. We are still in the process of making our algorithm more efficient so that we can conduct our analysis at temperatures lower than 994K. We present our results that we obtained as of this moment.

Figure 11 shows graphical representation of identified crystalline clusters at different temperature. There are more crystalline clusters growing independent of each other as compared to small system.
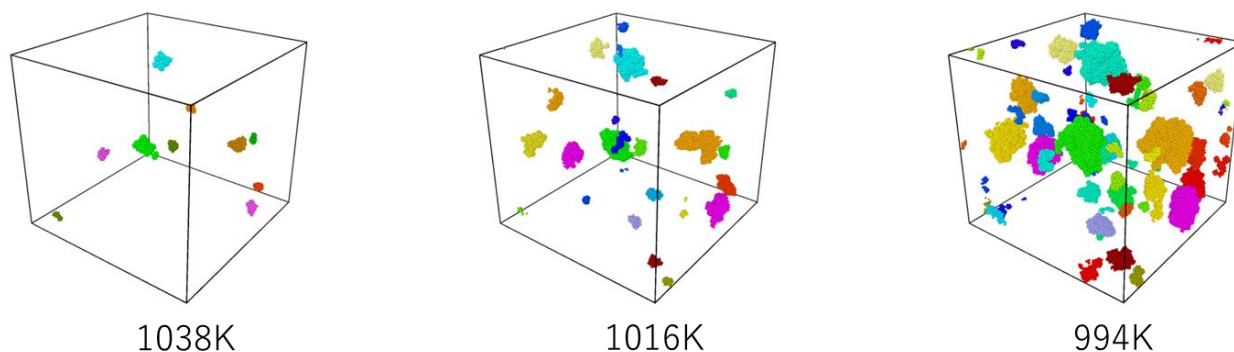

1038K   1016K   994K

Figure 11 Growing crystalline clusters in Zr20Al20Ni60 in large system.

Each crystalline cluster is colored differently.

In Figure 12 and Figure 13, we also shows results for large system from the same analysis as done for small system. We confirmed that same observation on FFLS and Voronoi Index for small system still holds in large system, at least to temperatures that we can reach as of this moment.
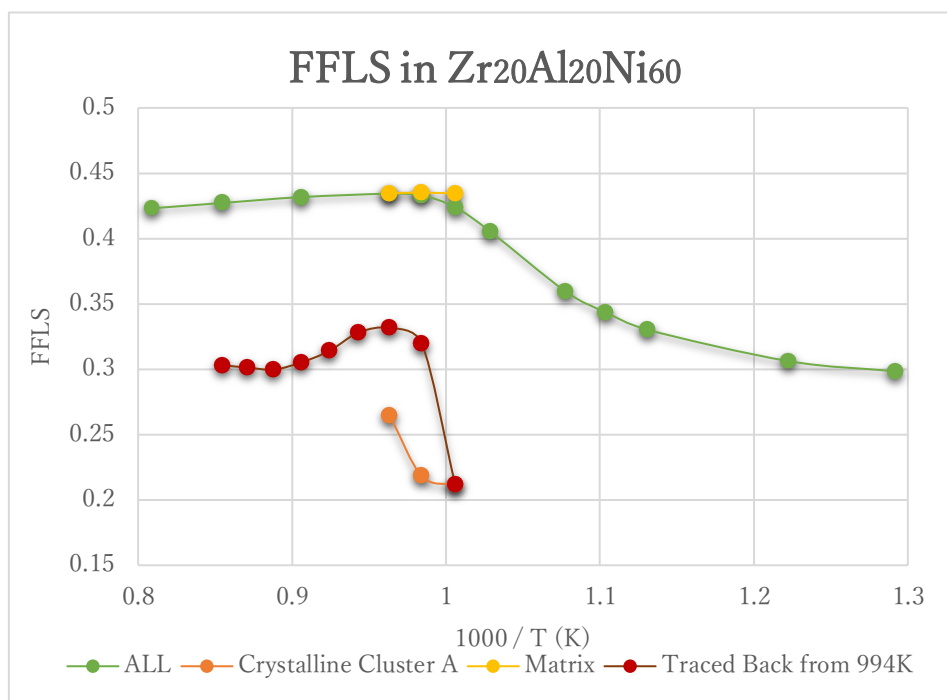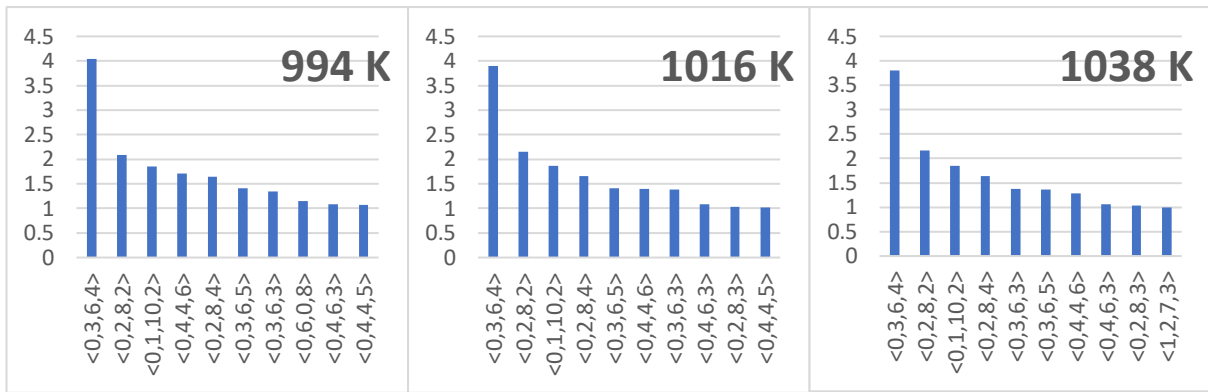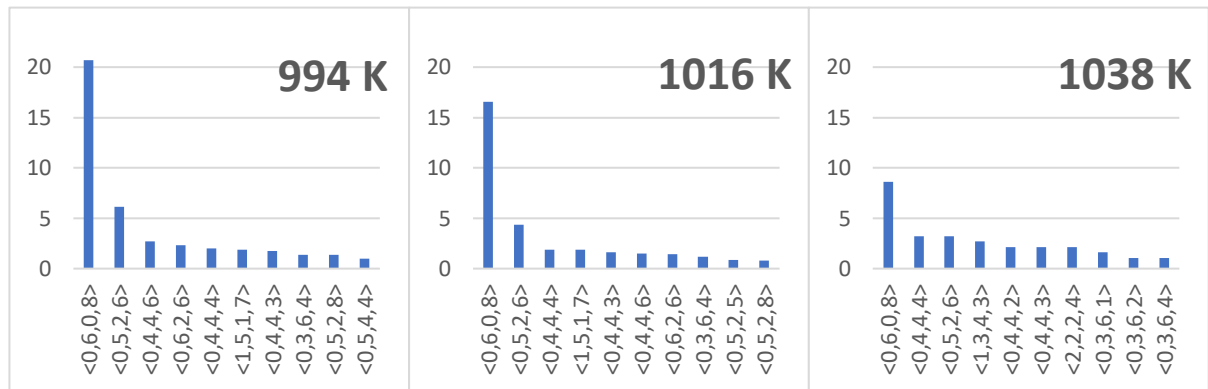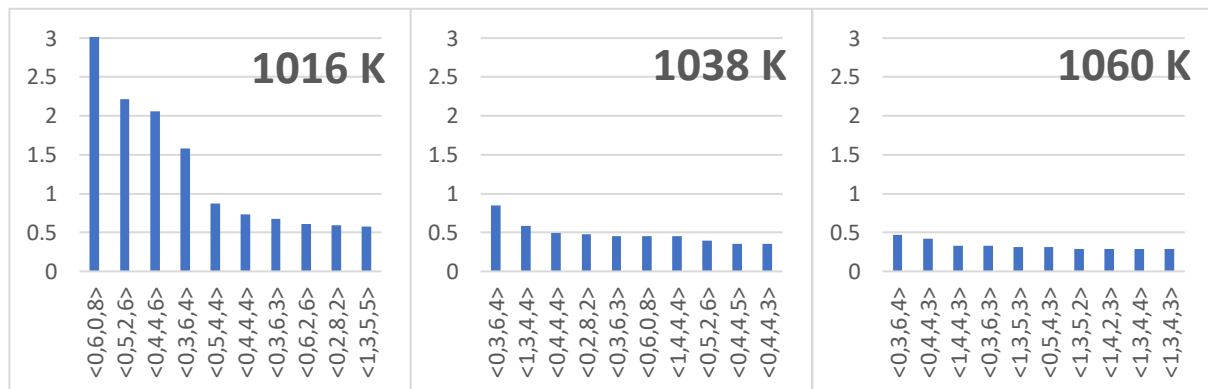

Figure 12. FFLS in Zr20Al20Ni60 in the large system

Voronoi analysis for all atoms in the large system

Voronoi analysis only for Crystalline Cluster A in the large system

Voronoi analysis only for traced atoms in crystalline cluster A at 994K

Figure 13. Voronoi analysises in the larger system.

Future Work

We plan to improve the efficiency of our program so that we can reach lower temperature below 994K in large system. When it is accomplished, we are ready to conduct similar analysis to slow-growing cluster and fast-growing crystalline clusters to better understand what makes such a difference at atomic level.

Acknowledgement

I would like to express my special thanks to Dr. Agrawal and Dr. Flores for the opportunity to this research and Juan Wang for all her help.

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