Predicting the Stable Structure of Solid-Solution High-Entropy Alloys using Atomistic Line Graph Neural Net for Force Field Prediction (ALIGNN-FF)

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Section 1 - Introduction

1.1 High-Entropy Alloys

The need for high-performance materials is ever-increasing in the problems facing today's world, as new materials are needed to create and store energy, make biodegradable products, better computers, and advanced aircraft and spacecraft. These applications (and many others) rely on material discovery and development to advance. A promising material type for use in high-performance applications is high-entropy alloys (HEA). HEAs are a relatively new development in materials science, being less than 20 years old. Nonetheless, they have already shown interesting and attractive properties such as extremely high melting temperature and fracture toughness, or very low thermal expansion[1]. They show remarkable mechanical properties and certain HEAs can outperform traditional engineering materials in both yield strength and fracture toughness (Figure 1)

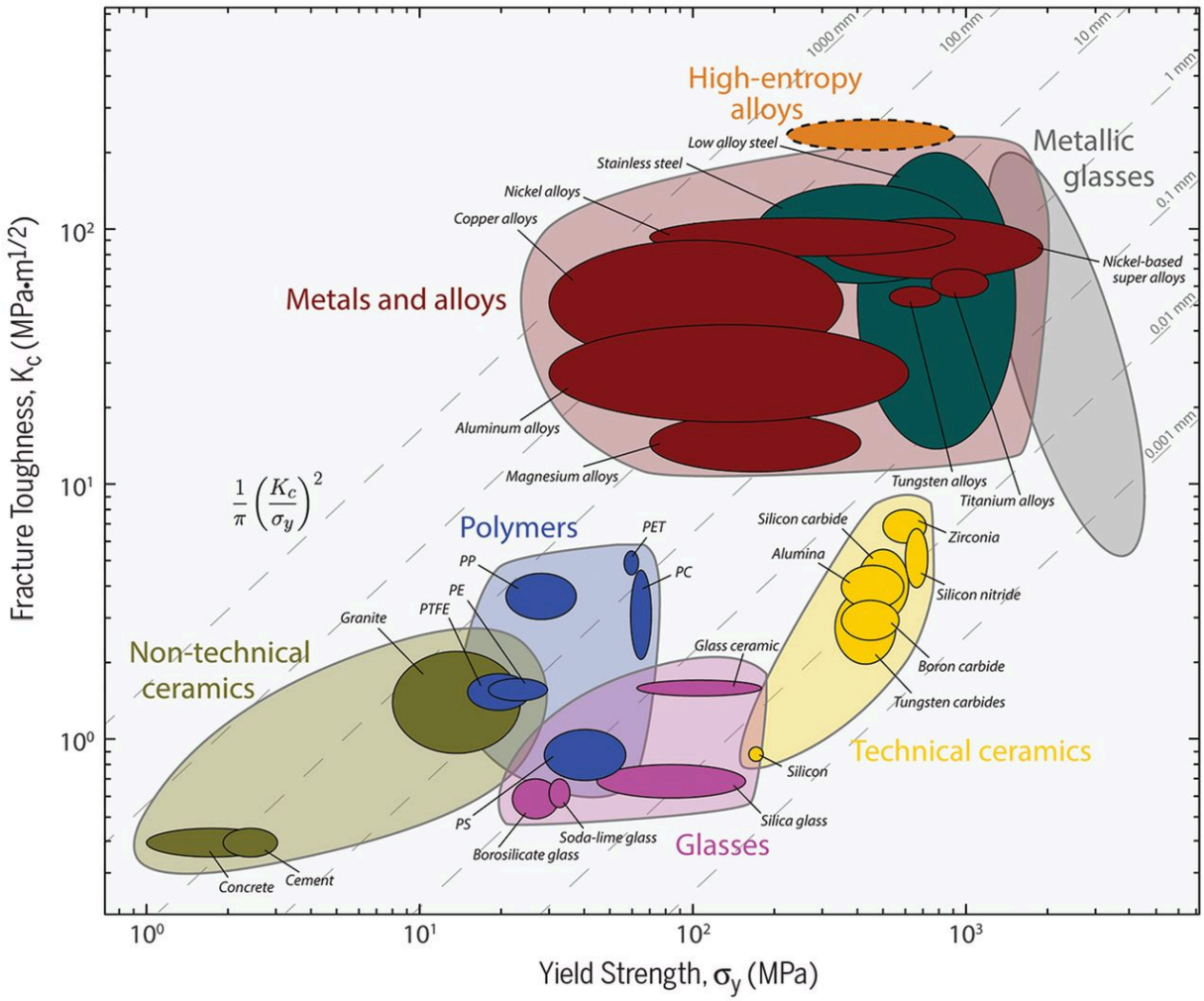

Figure 1: Ashby plot of different material families [2]

Whereas conventional engineering alloys like steel are composed of a single main element with much lower concentrations of alloying elements, HEAs are made of multiple principal elements (Figure 2 below). This distinction leads to the high configurational entropy that gives high-entropy alloys their name. It is important to note that HEAs also go by some other names, such as multi-principle-element alloys (MPEAs) or complex concentrated alloys (CCAs), but the name HEA will apply to any alloy composition near the equiatomic compositions in this paper for simplicity's sake.

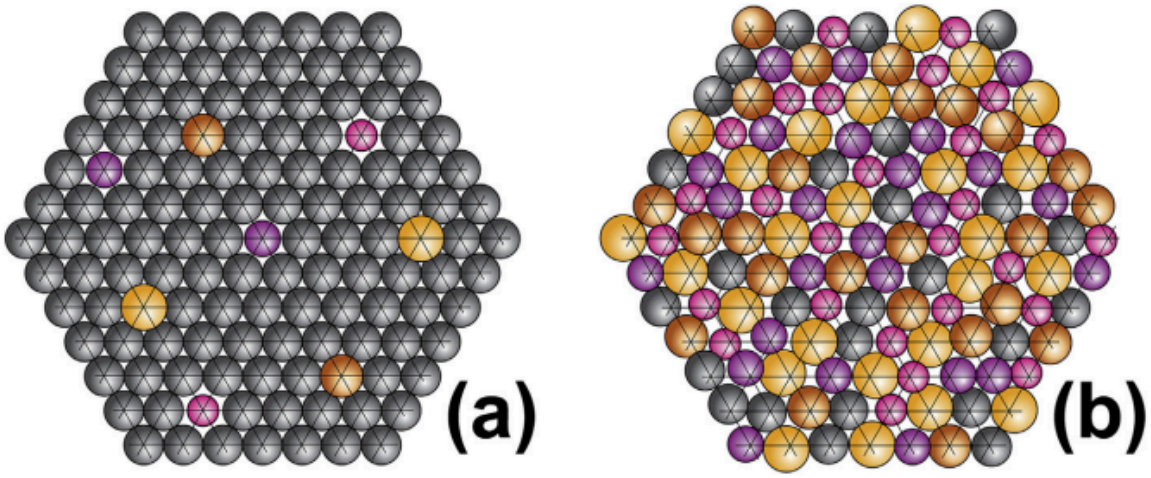

Figure 2: (a) Conventional engineering alloy, (b) HEA [1]

The complex nature of HEAs makes it hard to find general property relationships across the entire family of HEAs. An important problem in their study is finding HEA compositions that form solid solutions. In some compositions of HEAs with five or more major elements, the configurational entropy contribution to the total free energy in alloys may stabilize the solid-solution state[2]. However, HEAs very often form intermetallic compounds (precipitating phases) and are often too brittle for engineering use[1]. Predicting the microstructure and therefore behavior of HEAs is difficult using typical thermodynamic models due to their structural and entropic effects, so new effects must be used to analyze them. The four 'core effects' used to describe HEAs are lattice distortion, sluggish diffusion, high entropy, and the cocktail effect[1]. The cocktail effect specifically highlights one of the most interesting and complex aspects of HEAs and is a generalization of the complex relationships between their composition and microstructure. One aspect of this relationship is that HEAs don't always follow the Hume-Rothery solubility rules[1], which can add even more difficulty to their study.

1.2 Computational Study of HEAs

In the field of alloy design, the vast array of potential elements in HEAs makes traditional trial-and-error methods impractical. The compositional space of high entropy alloys exceeds 10^{50} unique combinations[3]. The massive combinatorial space of HEAs combined with the 'core effects' that describe them make their design and experimental exploration very difficult. To overcome these complexities, computational analysis techniques in Figure 3 have been used extensively to model the atomic-scale and bulk properties of HEAs. For example, one of the earliest theoretical studies on HEAs was a study on the relationship between solid solution stability, atomic size difference, and enthalpy of mixing[4]. This study applied the Hume-Rothery rule to investigate the formation of solid solutions in HEAs[5].

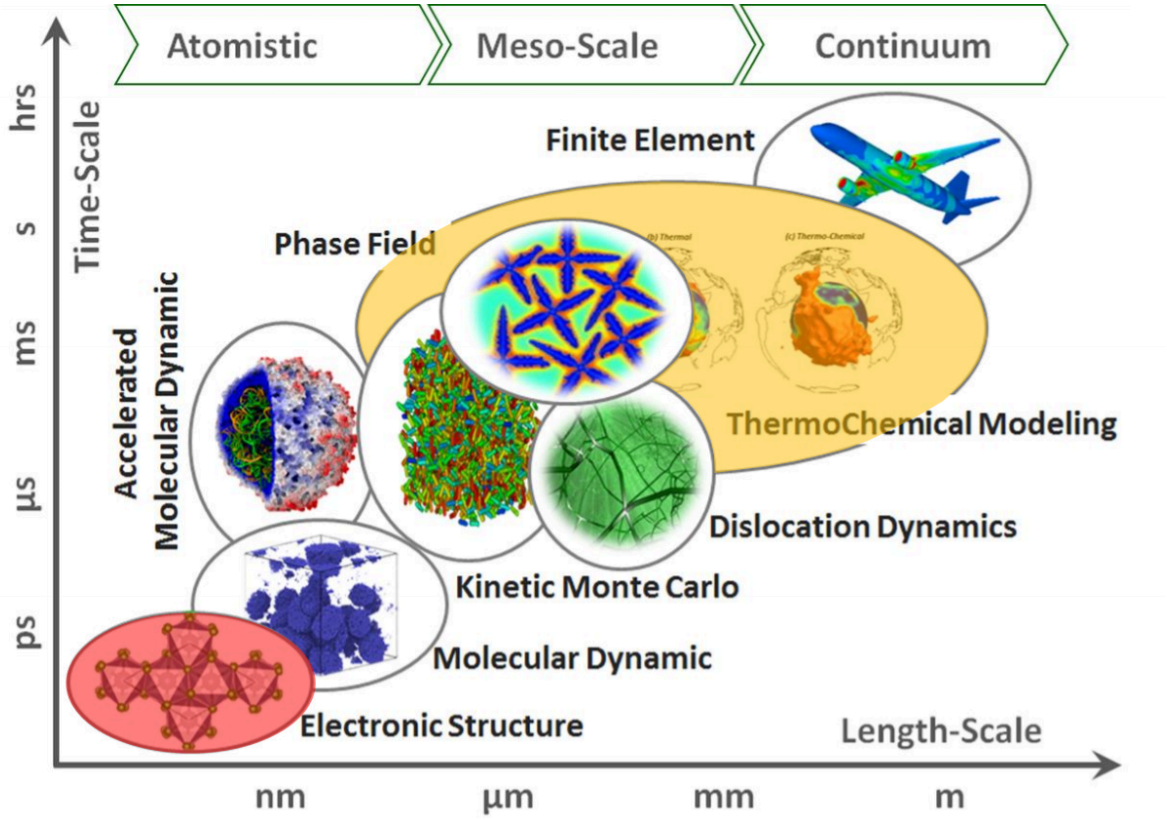

Figure 3: Multi-scale computational methods

The initial steps in computational materials design consist of calculating phase equilibria, predicting stable phases and crystal structures, and investigating the phase formations and transformations[3]. One of the most prevalent tools to do so is the self-empirical calculation of phase diagram method (CALPHAD) which is based on minimizing the free energy of the system. This software can predict the phase equilibria of HEA systems for those HEA systems that have an accurate literature CALPHAD database containing (excess Gibbs free energy of

mixing based on sublattice model)[6]. However, CALPHAD sometimes predicts more phases in the microstructures of HEAs than the experimental observations, and phases can also be over-predicted while some phases are neglected[3]. This is largely due to the current databases of Thermo-Calc being incomplete and therefore unable to generalize to the massive composition space of HEAs.

First-principle approaches like Density Functional Theory (DFT) and Molecular Dynamics (MD) are quantum-scale simulations based on individual atoms. They are used as theoretical tools to predict atomic structure and energy-based information. These approaches are the smallest scale simulations in the multi-scale computational materials framework and are known to be the most successful methods to study the electronic structures of materials[7].

DFT calculations can be used to assess the stability of different phases in HEAs, which is valuable for predicting an alloy's structural stability and its behavior under different conditions such as temperature and pressure. A limitation of this method is that the choice of exchange-correlation functionals and the treatment of certain electronic and thermodynamic effects can impact the accuracy of predictions[8]. Therefore, experimental validation is often necessary to confirm DFT predictions for high-entropy alloys. Additionally, the computational costs of DFT are very high, and ab initio molecular dynamics simulations are used instead to study the dynamic behavior of high entropy alloys at low temperatures.

MD can provide information about phase evolutions and structural properties of HEAs. Using combinations of thermodynamics and first-principles approaches has shown better promising results in studying HEAs. A critical drawback of MD is the unavailability of the necessary interatomic potentials, which need to be specifically developed for the target materials and temperature[3]. MD does not work without the correct interatomic potentials, but developing these potentials is time-consuming and computationally expensive.

Monte Carlo simulations are a broad range of computerized mathematical algorithms to study the probability of different objectives[9]. The large amounts of required data in Monte Carlo simulations usually increase the complexity of such simulations and make it harder to obtain results[3].

The main limitations of ab initio computational methods are their small scale (pm to nm), small number of atoms (a few hundred atoms), and relatively high computational costs compared to methods like CALPHAD[10]. For the simulation of a given alloy system using each method above, the alloy compositions have to be manually changed for each experiment, and it is often unknown whether the desired alloy composition would exist as a solid solution. This means that these processes are largely dependent on a trial-and-error approach and do not necessarily aid in developing interpretable trends that can be applied to the larger field of HEAs. Additionally, the

unique characteristics ('core effects') of HEAs cause some noticeable discrepancies between computational data and experiments. Due to this reason, even though the reviewed multi-scale computational tools have improved the research capabilities in studying and designing HEAs, they still have uncertainties and errors in modeling or calculations[3].

1.3 Machine Learning of HEAs

Machine learning (ML) is the computational task of adjusting the parameters of a function that maps an input to an output to minimize the error of doing so. There are many different types of machine learning approaches that operate on different principles and have better applications in their specific fields. The difficulty in predicting the properties and phases of HEAs means ML presents an incredibly promising opportunity for overcoming the complex, nonlinear relationships in HEA design.

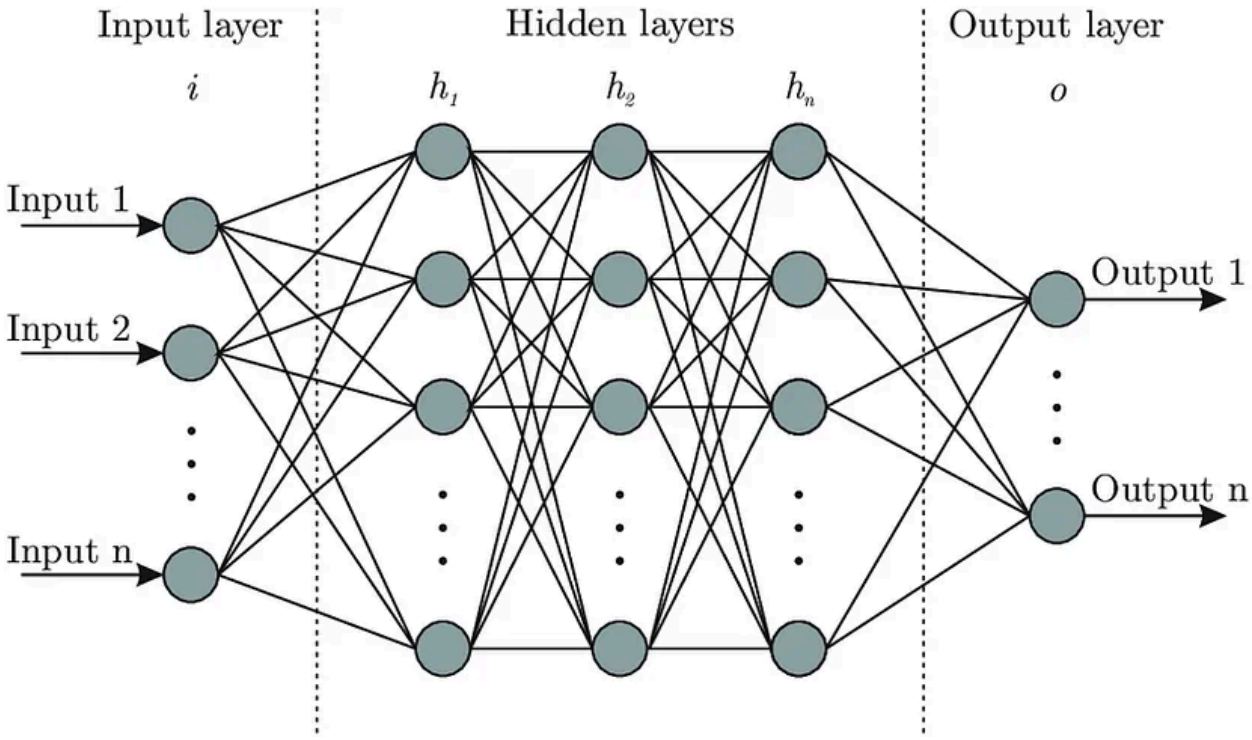

Figure 4: Neural network structure mapping inputs to outputs [11]

Neural network (NN) models (Figure 4) have been shown to successfully predict phase formations, microstructures, and mechanical properties of HEAs[12]. They can drastically reduce the need for time-consuming experimentation by predicting alloy properties[12-15] and finding new

alloy compositions with desired properties[16]. Additionally, NN-based methods are significantly more efficient for prediction in terms of computational efficiency than simulation methods and in some cases can offer higher accuracy[12,14]. However, it should be noted that some very large networks require long processing times and very large computational resources to train. All of the benefits of ML-based methods rely on the availability of good datasets[12]. If there is not enough data in a given dataset for a model to learn the relationship between the desired inputs and outputs, it will fail to capture the relationships in the actual system (underfit the data) and have unreliable performance. Conversely, a model can also be overfitted to a dataset such that it has incorporated measurement noise into its predictions, which also lowers predictive power. The nature of the prediction tasks in ML means that there will always be a degree of uncertainty in any prediction (seen in the loss of that network). This can potentially be a problem for predictions requiring high accuracy to be useful.

1.4 Graph neural networks (GNNs) for property prediction

Another downside of the ML methods discussed above is their failure to include atomic-scale interactions within crystalline systems. This is important to note, as the properties of materials are due to their atomic-level (and resultant mesoscale) structure. Crystal structures are naturally represented by graph structures (Figure 5a) in which atoms are nodes and bonds are edges. The application of convolutions (Figure 5b) to the graph representation can be used to implicitly represent the many-body interactions between atoms that predict properties of the original crystal structures and therefore map crystal structures to a desired property[17-19].

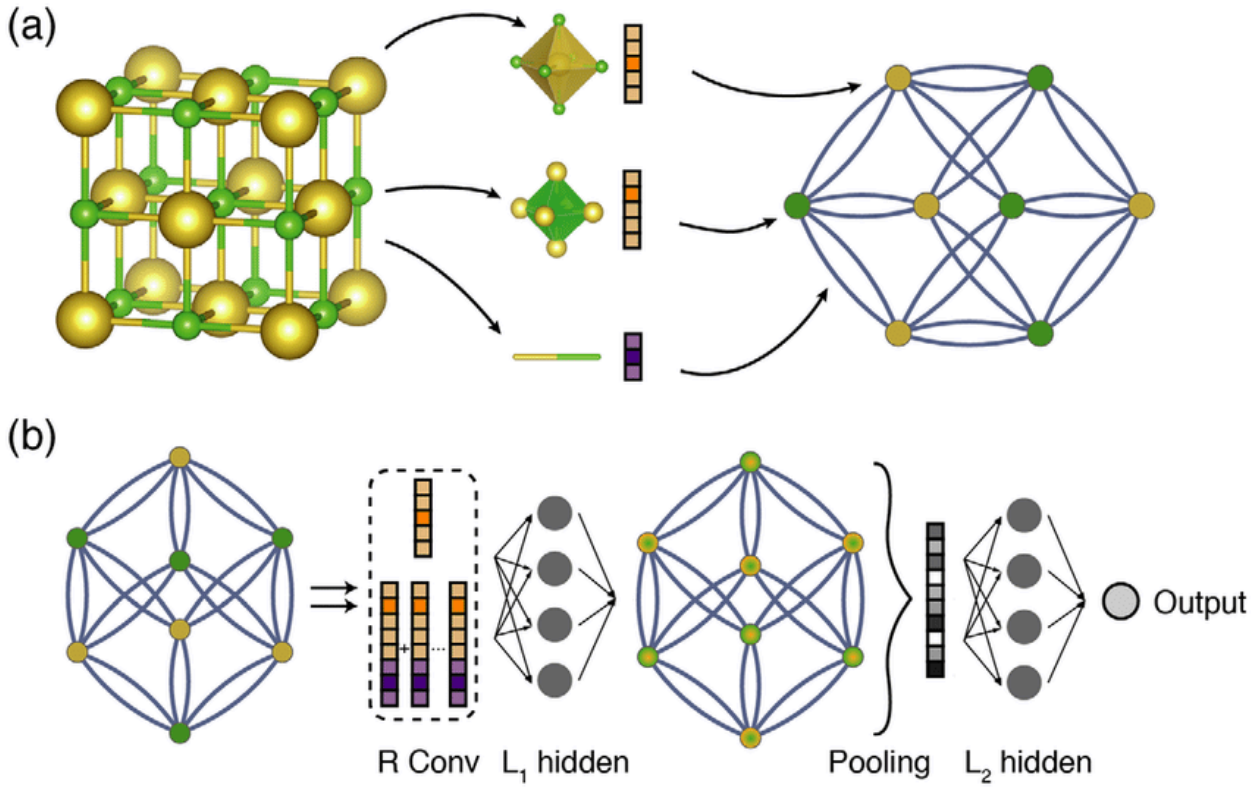

Figure 5: a. Graph representation of crystal structure where each atom is its own node and each local , b. Graph convolutions for property prediction - the mixing of colors after the convolution layer is indicative of the message passing in GNNs that allows for the implicit representation of atomic interactions [18]

Graph networks using this method have been shown to have the ability to accurately predict material properties at different scales such as band gap and elasticity[17-19]. GNNs have the added benefit of interpretability[18] in prediction since it is possible to see what atomic features are good predictors of various properties; this could be seen as analogous to the feature maps created by convolutional neural networks in the context of image recognition.

The Atomistic Line Graph Neural Network (ALIGNN) framework improves on the graph-based method by also including bond-angle information as a separate graph (line graph) derived from the atom-bond graph (Figure 6).

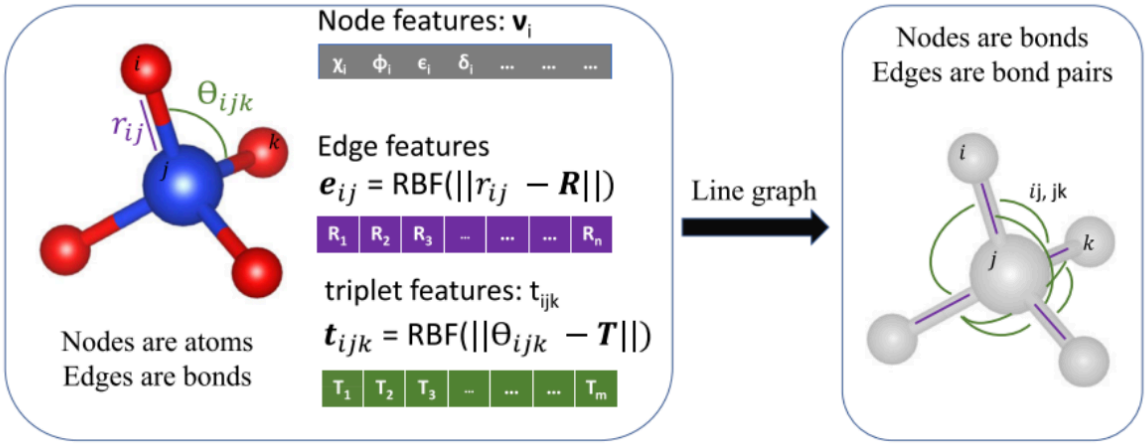

Figure 6: atom-bond graph (left) and corresponding bond-angle graph (right) [19]

Performing message passing (like convolutions) between the two graphs incorporates angle information into the local atomic neighborhood of the atom-bond graph, which is shown to significantly improve predictive performance[19]. It is vital to note that predictions using ALIGNN alone rely on an input of an accurate, relaxed crystal structure, and therefore ALIGNN by itself cannot predict equilibrium structure. However, it can be modified slightly to make the necessary predictions to discover stable compounds across the composition range of interest via the energy-driven discovery of convex hulls.

1.5 Force fields and convex hulls

In computational methods like MD, the force acting on each atom is described by interatomic potentials that take into account the many-body interactions within atomic systems to calculate the potential energy gradient at each lattice position[20]. Force fields are a type of interatomic potential that extends this idea to include other effects on potential energy like the electronegativity of each atom. The equilibrium crystal structure of an alloy is determined by the lowest energy configuration of its constituent atoms. Using a force field to find the total potential energy of all the atoms in a lattice, it is possible to determine the lowest-energy configuration and therefore equilibrium structure of those atoms. Doing this across the composition range of interest and then geometrically bounding the lowest energy points in the dataset allows for the creation of a convex hull plot (Figure 7).

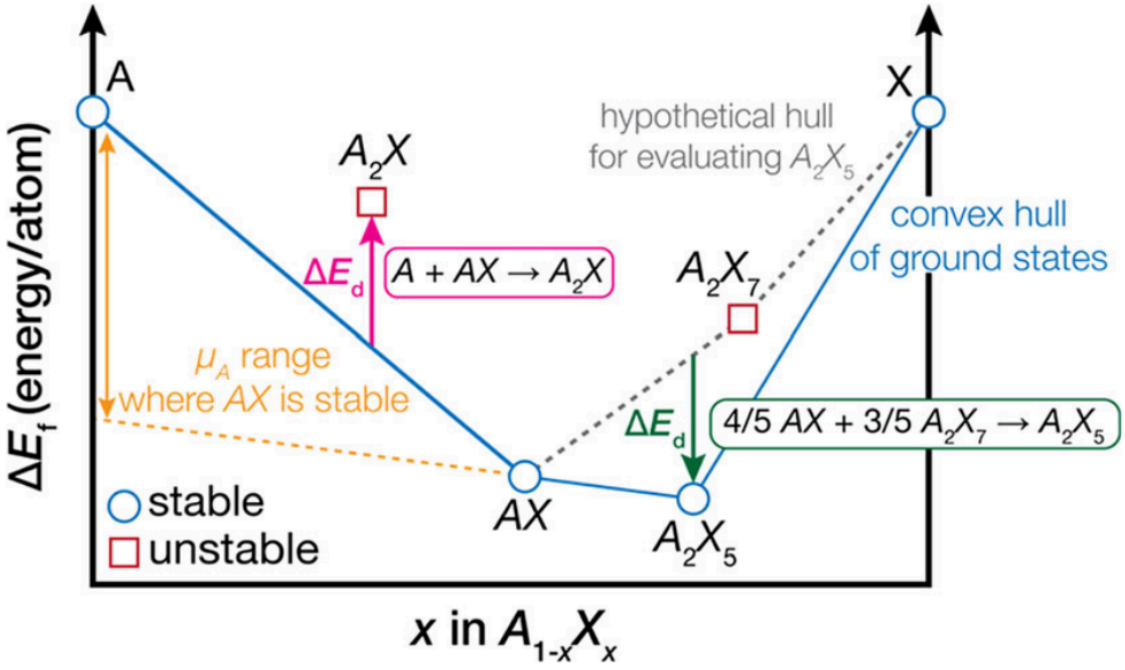

Figure 7: Representative convex hull plot for an arbitrary binary system A-X [21]

Convex hull plots contain a great deal of information about the phase structure of materials as they relate to lattice energy. Points that lie on the convex hull represent thermodynamically stable configurations that do not decompose into other compounds or undergo phase transitions[21]. Materials above the convex hull are metastable and can lower their energy either through a phase transition into another polymorph or by decomposing into a linear combination of alternative compounds with the same average composition[21]. Since solid-solution phases do not decompose into different phases (i.e. precipitate out intermetallic compounds), stability analysis via the convex hull should greatly narrow the search for solid solution HEAs.

1.6 ALIGNN-FF for convex hull prediction

ALIGNN-FF[22] is the application of ALIGNN to the prediction of the necessary derivatives to determine the force field acting on each atom in a local environment. This allows it to be used to find the relaxed crystal structures for arbitrary combinations of the 89 elements in its training data. This is critical to the computational study of alloys and importantly can be used in combination with a genetic algorithm (GA) to create convex hull plots for different alloys that show the lowest-energy (stable) compounds across the composition range of interest.

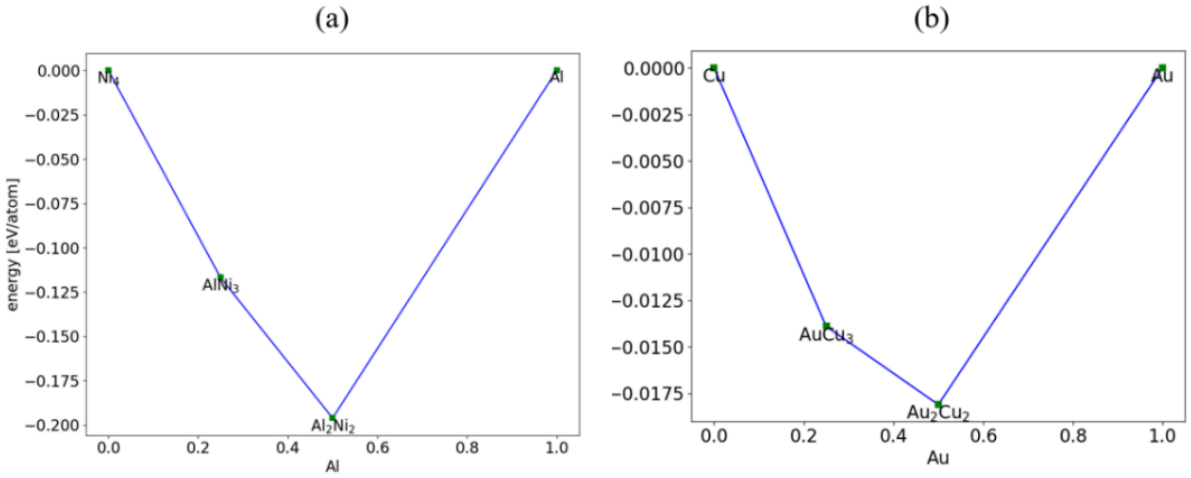

Figure 8: Generated convex hull plots for two test alloy systems [22]

Figure 8 above shows two test cases using ALIGNN-FF to make convex hull plots for Al-Ni and Au-Cu binary systems. The GA can successfully identify stable compounds across the respective binary composition ranges for both alloys[22]. Choudhary et al assert that this method should work for more complex systems than just binary alloys, and recognize that further testing on systems like HEAs needs to be done in separate research.

1.7 Research Focus

The focus of this research will be to apply the ALIGNN-FF and GA methods developed by Choudhary et al to HEA systems. For a given HEA system, a high-dimensional convex hull plot will be generated to find stable compounds across the composition range(s) of interest. Those stable compounds will be further analyzed using ALIGNN predictions to see if those compounds are solid-solution phases, and whether or not they match the literature composition and crystal structure for that composition. These central focuses lead to the research question this research will try to answer:

Can we use convex hull plots generated by ALIGNN-FF with a genetic algorithm to predict the solid solution compositions of the following HEA families? (where x is the alloy where the composition will be changed):

1. $Al_xCoCrFeNi$
2. Nb_xMoTaW
3. $V_xNbMoTaW$

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