3. COMPUTATIONAL METHODOLOGY

3.1 The Gupta Potential

The Gupta potential was originally designed to deal with inconsistencies between experimental data and computer simulation [65]. Now is used to model inter-atomic interactions in metal systems [66]. It is a semi-empirical many body potential derived within the tight-binding second-moment approximation. Many-body potentials advantage additive potentials in reproducing some basic properties for metallic systems.

The configurational energy of a cluster is written as the sum over all the atoms of attractive and repulsive energy components:

\[ V_{clus} = \sum_{i} \{ V^r(i) - V^m(i) \} \]

where the Born-Mayer pair repulsive term \( V^r(i) \) is expressed as:

\[ V^r(i) = \sum_{j \neq i} A(\alpha, \beta) e^{-p(\alpha, \beta)} \left( \frac{r_{ij}}{r_0(\alpha, \beta)} \right)^{-1} \]

and the many-body attractive term \( V^m(i) \) is expressed as:

\[ V^m(i) = \sqrt{\sum_{j \neq i} } \xi^2(\alpha, \beta) e^{-2q(\alpha, \beta)} \left( \frac{r_{ij}}{r_0(\alpha, \beta)} \right)^{-1} \]

\( \alpha \) and \( \beta \) represent the atomic species of atoms \( i \) and \( j \), respectively. \( A, \xi, p \) and \( q \) are the potential parameters that are usually fitted to experimental properties of bulk metals and alloys, such as the cohesive energy, lattice parameters, and independent elastic constants for the reference crystal structure at 0 K. \( r_0 \) denotes the nearest neighbor distance of the pure bulk elements, often taken as the average of the pure distances, but it can also be taken as the experimental nearest-neighbor distance in some specific ordered bulk alloy. \( r_{ij} \) is the distance between atoms \( i \) and \( j \) [65].
Values of the Gupta potential parameters describing Pt-Pt and Cu-Cu interactions are taken from the work of Cleri and Rosato [66]. These values are listed in the table below.

**Table 3. Gupta potential parameters [65].**

<table>
<thead>
<tr>
<th>parameter</th>
<th>Cu-Cu</th>
<th>Pt-Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>0.0855</td>
<td>0.2975</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>1.224</td>
<td>2.695</td>
</tr>
<tr>
<td>$p$</td>
<td>10.960</td>
<td>10.612</td>
</tr>
<tr>
<td>$q$</td>
<td>2.278</td>
<td>4.004</td>
</tr>
<tr>
<td>$r_0$</td>
<td>2.556</td>
<td>2.775</td>
</tr>
</tbody>
</table>

### 3.1.1 Parameterization of the Gupta Potential

A previous study on nanoalloys concluded that parameters obtained by averaging the parameters of pure elements, gave a good qualitative fit to previous experimental and theoretical studies of bimetallic clusters [67]. In this study, the heteronuclear Cu-Pt Gupta potential parameter set $\{P\}$ is derived as the weighted average of the corresponding pure metal Cu-Cu and Pt-Pt parameters:

$$P(\text{Cu-Pt}) = w_1P(\text{Cu-Cu}) + w_2P(\text{Pt-Pt})$$

Weighting parameters have been investigated in the range $0 \leq w \leq 1$, in steps $\Delta w = 0.1$. This is called symmetrical weighting of all parameters, since all of the parameters vary in the same way. That is, from the value for Pt-Pt ($w = 0$) to the value for Cu-Cu ($w = 1$) [52]. Therefore, the Gupta potential parameters $\{P\} = \{A, \zeta, p, q, r_0\}$ are obtained as:

$$P(\text{Cu-Pt}) = wP(\text{Cu-Cu}) + (1 - w)P(\text{Pt-Pt})$$
Table 4. Parameter set values.

<table>
<thead>
<tr>
<th>( w )</th>
<th>0.0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>0.2975</td>
<td>0.2763</td>
<td>0.2551</td>
<td>0.2339</td>
<td>0.2127</td>
<td>0.1915</td>
<td>0.1703</td>
<td>0.1491</td>
<td>0.1279</td>
<td>0.1067</td>
<td>0.0855</td>
</tr>
<tr>
<td>( \zeta )</td>
<td>2.695</td>
<td>2.548</td>
<td>2.401</td>
<td>2.254</td>
<td>2.107</td>
<td>1.960</td>
<td>1.812</td>
<td>1.665</td>
<td>1.518</td>
<td>1.371</td>
<td>1.224</td>
</tr>
<tr>
<td>( q )</td>
<td>4.004</td>
<td>3.831</td>
<td>3.659</td>
<td>3.486</td>
<td>3.314</td>
<td>3.141</td>
<td>2.968</td>
<td>2.796</td>
<td>2.623</td>
<td>2.451</td>
<td>2.278</td>
</tr>
<tr>
<td>( r_0 )</td>
<td>2.775</td>
<td>2.753</td>
<td>2.731</td>
<td>2.709</td>
<td>2.687</td>
<td>2.666</td>
<td>2.644</td>
<td>2.622</td>
<td>2.600</td>
<td>2.578</td>
<td>2.556</td>
</tr>
</tbody>
</table>
3.2 The Birmingham Cluster Genetic Algorithm

The Birmingham Cluster Genetic Algorithm (BCGA) is a program that has been used to find the putative local minima as well as other low-lying energy structures [78]. The operation of this GA optimization program is shown in figure 10.

![Flow chart for the BCGA program](image)

**Figure 10.** Flow chart for the BCGA program [47,48].
For a given cluster size ($N$), a number of clusters, ($N_{pop}$, typically from 10 to 30) are generated at random to form the initial population. The $x$, $y$ and $z$ coordinates are real values on the Cartesian space [49]. These values are chosen randomly in the range $[0,N^{1/3}]$ [47]. This ensures that the cluster volume scales correctly with cluster size (i.e. linearly with $N$). All of the clusters in the initial population are then relaxed into the nearest local minima, by minimizing the cluster potential energy as a function of the cluster coordinates, using the quasi-Newton L-BFGS routine [50,51].

As the cluster GA is being used to minimize the cluster potential energy ($V_{clus}$), the lowest energy clusters have the highest fitness and the highest energy clusters have the lowest fitness.

Dynamic scaling is achieved by using a normalized value of the energy, $\rho$, in the fitness calculations:

$$\rho_i = (V_i - V_{min})/(V_{max} - V_{min})$$

where $V_{min}$ and $V_{max}$ are the lowest and highest energy clusters in the current population, respectively. The most common fitness functions that have been used are:

Exponential:

$$f_i = e^{-\alpha \rho_i}$$

where $\alpha$ is typically set to 3.

Linear:

$$f_i = 1 - 0.7 \rho_i$$

Hyperbolic tangent:

$$f_i = \frac{1}{2} [1 - \tanh(2\rho_i - 1)]$$

The choice of fitness function controls how rapidly fitness falls off with increasing cluster energy.
The selection of parents is accomplished using either roulette wheel or tournament selection. In both of these selection schemes, low energy clusters are more likely to be selected for crossover and therefore to pass their structural characteristics on to the next generation. Once a pair of parents has been selected, they are subjected to the crossover operation.

Crossover in this implementation consists of random rotations that are performed on both parent clusters and then both clusters are cut horizontally about one or two positions parallel to the $xy$ plane, and complementary fragments are spliced together. For the single cut method, the cutting plane can be chosen at random; it can be defined to pass through the middle of the cluster, or weighted according to the relative fitness of the two parents. For the double cut method, the cutting planes are chosen at random.

Crossover continues until a predetermined number of offspring ($N_{off}$) have been generated. The number of offspring is generally set to approximately 80% of the population size. Each offspring cluster is subsequently relaxed into the nearest local minimum, as described above. The local minimization step obviously changes the structure of the offspring cluster, and this structural rearrangement will be greatest in the region of the join between the two fragments donated by its parents. As the clusters get larger, however, the perturbation due to the local minimization should become relatively smaller and confined to the join region. In this way, the principle of schemata should apply, as parents with high fitness are more likely to have fit offspring by passing on fragments with low energy arrangements of atoms.

![Figure 11](image)

**Figure 11.** Schematic representation of the Deaven–Ho cut and splice crossover operation, as implemented in our GA program. (Single cut crossover is shown) [47].
In an attempt to avoid stagnation and to maintain population diversity, a mutation operator is introduced, whereby each individual has a probability \( P_{\text{mut}} \) of undergoing mutation. The mutation perturbs some or all of the atoms within the cluster.

Some of the mutation schemes that can be adopted include: atomic displacement, twisting, cluster replacement, atom permutation. After mutation, each “mutant” cluster is subsequently relaxed into the nearest local minimum, using the L-BFGS minimization routine.

The new population is selected from the \( N_{\text{pop}} \) lowest energy clusters selected from the set containing the old population, the new offspring clusters and the mutated clusters. The inclusion of clusters from the previous generation makes the GA elitist, ensuring that the best member of the population cannot get worse from one generation to the next.

Once the new generation has been formed, the potential energies of the best \( V_{\text{min}} \) and worst \( V_{\text{max}} \) members of the population are recorded and the fitness values calculated for the entire population. The whole process of crossover, mutation and selection is then repeated for a specified number \( N_{\text{gen}} \) of generations or until the population is deemed to have converged. The population is considered to be convergent if the range of cluster energies in the population has not changed for a prescribed number of generations [47].

A considerable amount of effort has been expended in optimizing the GA operations and parameters described above [52]. Because of the stochastic nature of the GA, the GA program is run several times for each cluster’s nuclearity and for each set of operations/parameters. It is generally found that there is not a great dependence of the success rate of finding the global minimum structure on the type of fitness function used, though even small improvements are useful, especially for larger cluster sizes. For larger clusters, a larger population size and maximum number of generations is generally required [47].

In our instance we use the convergence criterion limited to a maximum of 400 generations and a population of 40 clusters. For a given cluster size, 38 in our case, coordinates of the atoms are randomly generated and normalized.
3.3 Energetic Analysis

When studying fixed-size bimetallic clusters, the excess (or mixing) energy as a function of composition, $\Delta N$, is a useful quantity. For binary nanoalloys with fixed size (N = 38 atoms) but different compositions, $\Delta N$ is defined as:

$$\Delta N = E_N(A_M B_{N-M}) - M \frac{E_N(A_N)}{N} - (N - M) \frac{E_N(B_N)}{N}$$

where $E_N(A_M B_{N-M})$ is the total energy of a given cluster calculated at the Gupta level and $E_N(A_N)$ and $E_N(B_N)$ are the total energies of the global minima of the pure metal clusters (i.e. Cu$_N$ and Pt$_N$) [52]. This excess energy is an unbiased quantity, defined as zero for the global minima of the pure clusters. Negative values of $\Delta N$ indicate that mixing is favorable.

3.4 Chemical Ordering

Binary nanoalloys generally present more complex structures than monometallic clusters and global optimization is more difficult due to the existence of homotops [6], which are isomers with the same geometry and composition but with a different arrangement of the two types of atoms. For an A-B alloy system, the chemical order parameter, $\sigma$ is defined as:

$$\sigma = \frac{N_{A-A} + N_{B-B} - N_{A-B}}{N_{A-A} + N_{B-B} + N_{A-B}}$$

where $N_{A-B}$ is the number of nearest-neighbor A-B bonds and $N_{A-A}$ and $N_{B-B}$ denote the numbers of homonuclear bonds in the binary cluster [69]. The $\sigma$ value is positive when cluster segregation occurs, close to zero when disordered mixing takes place, and negative when there is more ordered mixing including layering and onion-like configurations [16].
3.5 Density Functional Theory

DFT calculations were performed using the NWChem quantum chemistry package [70] and the Perdew-Wang exchange-correlation functional (PW91) [71,72]. The electronic exchange energy as a functional of the density may be approximated as:

\[ E_x[n] = A_x \int d^3r \, n^{4/3} F(s) \]

where:

\[
s = \frac{[\nabla n]}{2k_F n}, \quad k_F = (3\pi^2 n)^{1/3}, \quad F(s) = (1 + 1.296s^2 + 14s^4 + 0.2s^6)^{1/15}\]

Unlike most other functionals this one is simple enough to be applied routinely in self-consistent calculations for atoms, molecules and solids. On the other side is important to note that the self-consistent valence electron density in an atom is still somewhat too diffuse [71].

Often due to the limited accuracy of semiempirical potentials, DFT reoptimization may significantly change the energetic ordering of clusters belonging to different structural motifs [73]. In order to verify this possibility we chose low energy structures generated by the BCGA and performed reoptimization calculations.

3.6 Pair Distribution Function

The PDF gives the probability of finding two atoms separated by a distance \( r \) [74]. This function is obtained by integrating the distribution functions over the positions of all atoms excluding the two atoms measured. We must also include appropriate normalization factors. We use a definition that takes into account the averages over the ensemble atom pairs which is useful in computer simulations [75].

\[
g_p(\vec{r}) = \frac{V}{N^2} \left( \sum_i^N \sum_{j \neq i} \delta[\vec{r} - \vec{r}_{ij}] \right)
\]
The PDF is important because it allows the characterization of the lattice structure of the nanoalloys [76]. In our study we use it to structurally compare the motifs generated using the BCGA technique and the motifs that have been reoptimized with the DFT method. This allows an objective and quantitative comparison of the structures.