important lower energy configurations (Fig. 5.15). This provided the motivation for the development of the hybrid GA-MD based methodology to ensure the sampling low energy configurations.

5.6 Development of a hybrid genetic algorithm-MD (GA-MD) method

Genetic algorithm (GA) is one of the evolutionary algorithms used for solving stochastic sampling and optimisation problems. It derives its methodology from evolution theory, where individuals (parents) mate to generate children. Only those individuals survive which meet selection criteria and gradually the system progresses towards a population with fittest individuals. GA was initially employed by Holland [65] for solving computational problems. This technique has been applied to study the range of optimisation [66–69] and sampling [70] problems. The goal of the present work is to develop a sampling methodology for multicomponent positional-disordered materials. Before we delve into details of the sampling procedure, the functional components of GA method need to be understood. As has been mentioned above, the information is shared between two GA individuals (i.e., parents) by the process of mating or crossover. For crossover to take place, information of parents needs to be encoded. There are several encoding schemes, *e.g.*, binary encoding, permutation encoding, value encoding, tree encoding, etc. The selection of encoding scheme is dependent upon the problem of interest and details of such encoding schemes are beyond the scope of present work. In the present work, we have employed permutation encoding as the information which will be swapped between GA individuals is the coordinates of atoms at lattice points

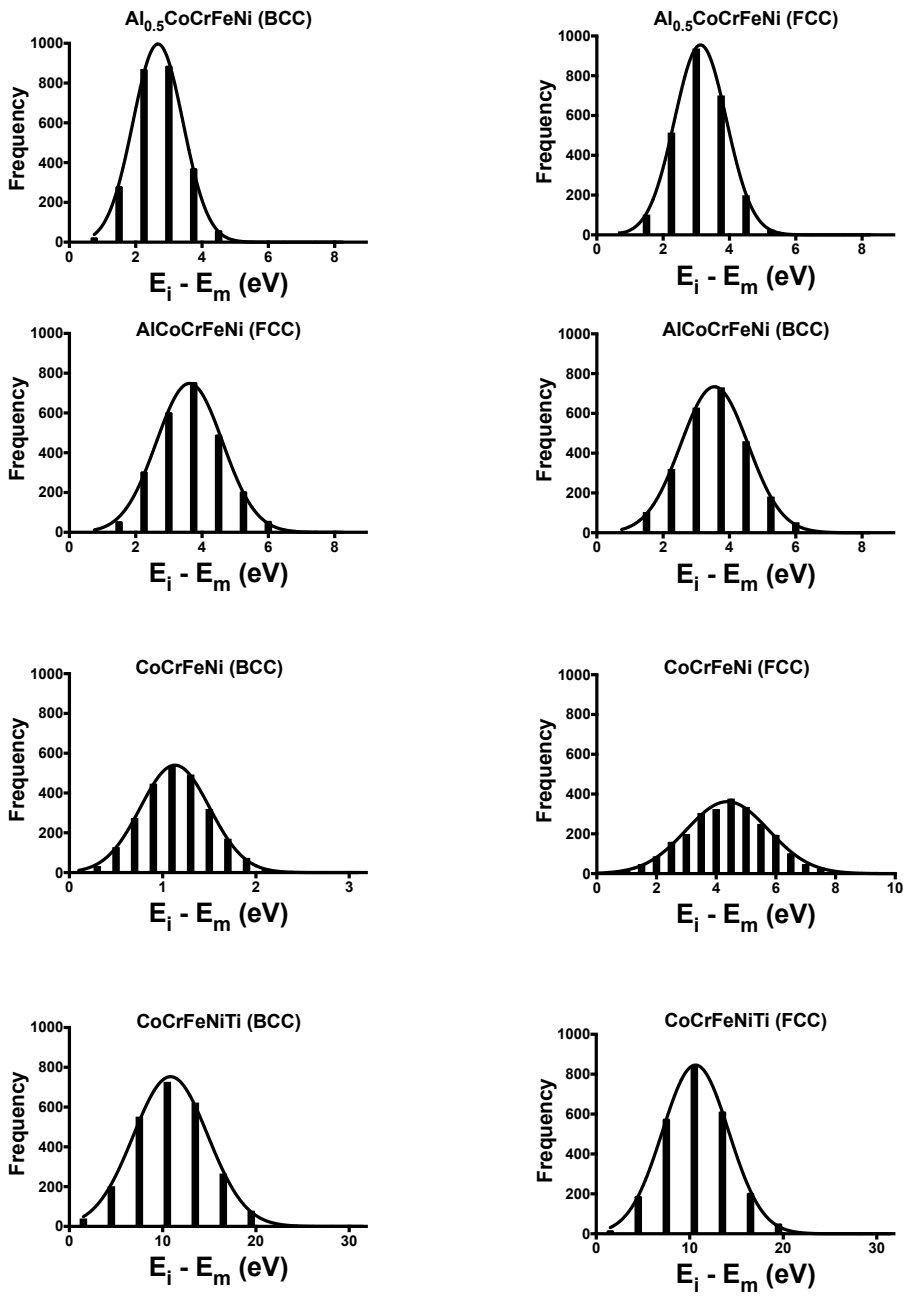

Figure 5.15: The distribution of configurational energy for different alloys. E_m represents minimum energy among 2500 random configurations, while E_i is energy of i^{th} configuration. Note that energies are for whole supercell. Curves in the figures are fitted Gaussian distributions.

and permutation encoding is suitable scheme for problem in hand.

Once, the encoding is done, the selection of parents in GA is carried out. This stage of parent population generation is basically a stochastic selection mechanism, which ensures survival of the fittest by removing less fit individuals from the parent population. After the generation of the parent population, the information between GA individuals is swapped by *cross-over* and in the last stage certain random changes in children are allowed, which is termed *mutation*.

The present sampling approach should ensure that swapping of information between two configurations (i.e., parents) leads to inheritance in new configurations (children), as shown in Fig. 5.16. Another important constraint which needs to be applied while generating new configurations concerns with the maintenance of constant composition of the supercell during sampling. The steps of GA-MD procedure developed can be stated as:

1. Initially, the 100 configurations with the lowest energies are chosen from 2500 randomly generated configurations.

2. Generate a random number (say x) between 1-1024. If $1 \leq x \leq 511$, then choose any configuration number 1 to 10, if $512 \leq x \leq 767$, the choose any configuration number 11 to 20, if $768 \leq x \leq 895$, then choose any configuration number 21 to 30, if $896 \leq x \leq 959$, then choose any configuration number 31 to 40, if $960 \leq x \leq 991$, then choose any configuration number 41 to 50, if $992 \leq x \leq 1007$, then choose any configuration number 51 to 60, if $1008 \leq x \leq 1015$, then choose any configuration number 61 to 70, if $1016 \leq x \leq 1019$, then choose any configuration number 71 to 80, if $1019 \leq x \leq 1023$, then choose any configuration number 81 to 90 and if $x = 1024$, then choose any configuration number from 91 to 100 randomly.

3. Once a list of 100 configurations are chosen, these act as reservoir of parents for particular GA generation.Two parents are chosen sequentially, i.e., configuration number 1 and 2 are chosen to be parent 1 and parent 2 respectively, configuration number 3 and 4 are chosen to be parent 3 and parent 4, respectively and so on. Note that swaps between consecutive parents are carried out, i.e., parent-1 and parent-2, parent-3 and parent-4, etc.

4. Swapping between configuration files is carried out as shown in Fig. 5.17 and steps in such a swap process are shown in Fig. 5.18. Firstly, the number of swaps is decided to be randomly in between 10-30%. In each swap: a random number (i) between 1 and N (number of atoms in the supercell) is generated, which corresponds to the particular atom and its coordinates. It is important to note that configuration files are generated in a way such that list of atomic symbols in both the files are in same order. So, the i^{th} position in both files corresponding to parent-1 and parent-2 corresponds to same atomic species, also shown in Fig. 5.18(a). After finding the coordinate of the i^{th} atom in both parent-1 and parent-2, which are (X_A, Y_A, Z_A) and (X_B, Y_B, Z_B) respectively, the identity of atomic species at (X_B, Y_B, Z_B) in parent-1 and identity of the atomic species at (X_A, Y_A, Z_A) in parent-2 is determined. It is demonstrated for sake of understanding in Fig. 5.17 and also in Fig. 5.18(b), that in parent-1 the atomic species in question is Fe (j^{th} position in configuration file of parent-1) and Co in case in parent-2 (k^{th} position in configuration file of parent-2). In the next stage, swapping between the i^{th} and j^{th} positions in the configuration file of parent-1 and the i^{th} and k^{th} positions in the configuration file of parent-2 is carried out (Fig. 5.18(c)), which leads to a change in the atomic configurations in both parent-1

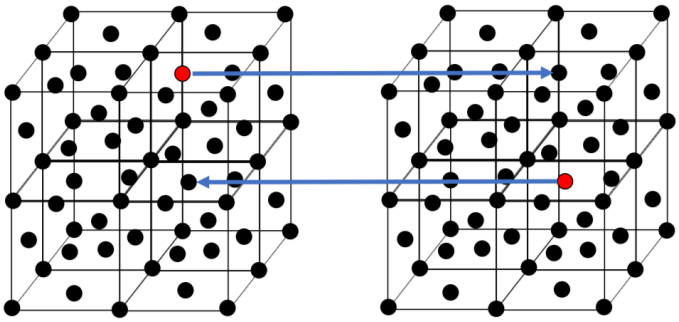

Figure 5.16: Schematic representation of the aim of the swapping process to ensure that swapping leads to inheritance of information regarding the identity of atom at equivalent positions.

and parent-2. Note that in Fig. 5.18(d), the new configuration from parent-1 has inherited Cr atom (red dot) where a Cr atom was present in the case of parent-2, while the same is the case for the new configuration generated from parent-2. Such a swapping process is repeated several times, lying between 10-30% of the total number of atoms in the supercell. Also one swap lead to an associated mutation, i.e., Fe atom (green) is at the position, where Cr was initially present in the case of parent-1, while a Co atom (blue) is present at the position, where Cr was present initially.

5. After the generation of 100 new children configurations, MD relaxation is carried out for each of these configurations and their energy is stored.

6. The reservoir of parents for the next generation is chosen again using the process depicted above in step 2.

7. The process depicted from step 2 to step 5 is repeated until all the energies from 100 configurations exhibit the same value.

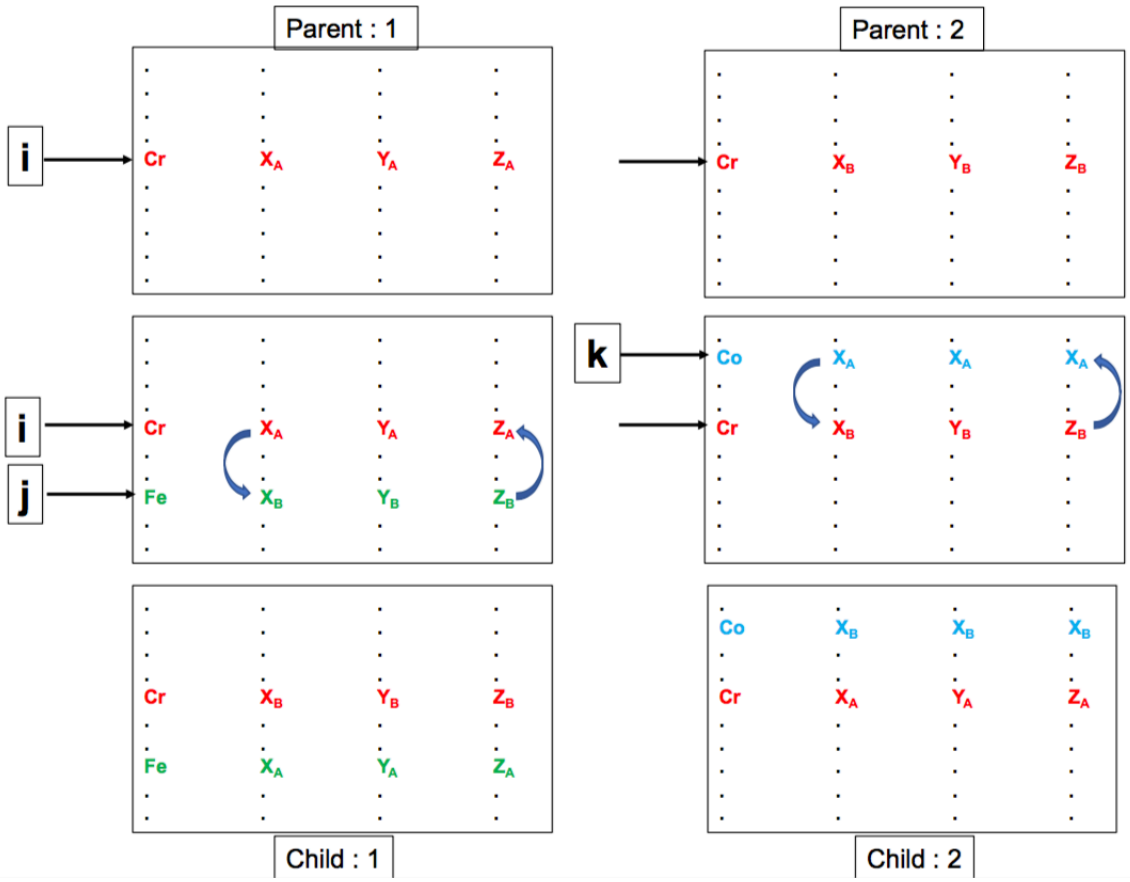

Figure 5.17: Schematic representation of the swapping in configuration files of parents.

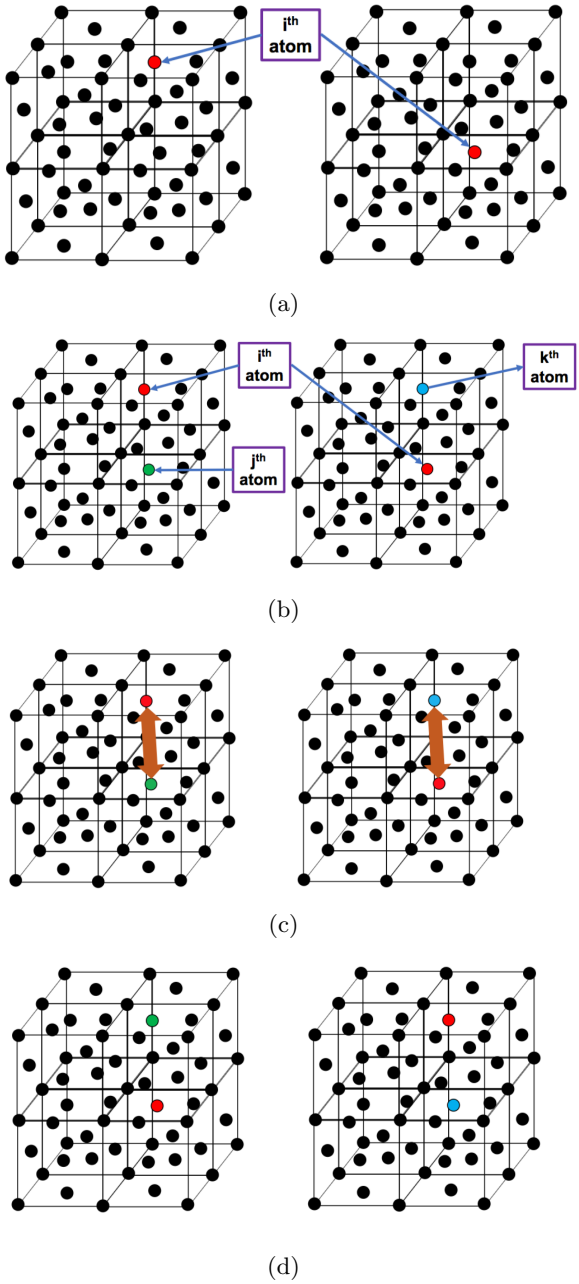

Figure 5.18: Schematic representation of the swapping process.

Element	Configurational energy (eV/atom)
Al	-3.541326
Co	-4.532784
Cr	-3.982647
Fe	-4.251920
Ni	-4.495262
Ti	-4.889643

Table 5.5: Configurational energy values for elements.

It is important to note that, once the energy variation in the population had reached zero (all configurations had the same energy), then further sampling was unlikely to improve the population in terms of finding lower energy configurations. Therefore, this provided the rationalisation to stop the GA-MD cycle.

Figure 5.19 shows that 61 and 71 generations of a GA-MD cycle are required for the BCC and FCC variants of $Al_{0.5}$CoCrFeNi to reach the state, when all the configurations have equal energy. For AlCoCrFeNi, the BCC and FCC phases both required 77 cycles. For BCC-CoCrFeNi, 71 generations were required, while 82 cycles were required for the FCC variant. 55 and 56 generations were required for BCC and FCC variants of CoCrFeNiTi, respectively. It should be noted that the BCC variant reaches the state when all the configurations have same energy before the FCC variants in all the cases, which is surprising since the number of atoms simulated in the BCC (1458 atoms) was slightly higher than the FCC (1372 atoms).

5.7 Gibbs free energy calculation

The expression for Gibbs free energy (G) employed in the in the present work has been obtained from Allan *et. al.* [16], where it is expressed for an isothermal-isobaric