Classic Study on the Growth of Metal Clusters Al_xNa_{N-x} ($3\leq N \leq 55$) Using Genetic Algorithms Modeled by the Gupta Potential

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Introduction

As a new area of research, nanoscience has been in development since the 1980s. Its main scope is the study of nanoscopic phenomena (1nm = 10-9m), where clusters refer to a new type of materials (nanoparticles), in the order of 2 to 10n (n = 6 or 7) atoms or molecules. These particles may be identical or related to two or more distinct species: monoatomic and monomolecular clusters, polyatomic and/or polymolecular clusters, or molecular clusters. Clusters consisting of a small amount of atoms (2-1000 atoms) are denominated nanoclusters. Such systems are adequate models of researching by the means of theoretical methodologies, as they have a smaller number of particles. On the other hand, they may present difficulties regarding experimental studies, such as structural determination.[1]

Theoretical studies concerning clusters are relevant and contribute to the interpretation of experimental measures. Among these studies, we may find those that determine the structures of atomic and/or molecular clusters, possibly using mathematical tools related to spatial geometry applied according to theoretical models. Besides, the quantitative study of potential energy provides us with the basis for the understanding of chemical and physical phenomena of atomic and molecular clusters.[2]

Particularly, the determination of isomers of greater cluster stability has ample relevance to the development of new materials, where the more stable structure of cluster corresponds to that of lower energy. In order to determine the cluster structure and energies, one should calculate the conformation of lower energy on the potential energy surface (PES), i. e. the global minimum (GM). Generally, the determination of a minimum is considered an optimization problem. The sheer number of isomers with diverse structures constitute one of the chief difficulties in the determination of the GM in PESs, where it may be verified that there is an almost exponential growth in the number of minimum structures related to the number of particles, i. e., the system size[3,4]. Therefore, optimization methods have been developed in order to contribute to the above-mentioned difficulties, whether they are biased or non-biased. The former utilize chemical or physical information regarding the material and initial conditions such as starting geometry, whilst the latter, in contrast, does not use previous information, and the initial geometry is instead defined at random and thus optimized until a minimum of lower energy is found.

This current study proposes the application of non-biased methods, since they may reduce the occurrence of problems such as the determination of local minima, which are recurring in other methods due to the imposition of certain types of geometries or of a PES region. The non-biased methods of optimization have two instruments that may be considered the most effective overall: 1) the exhaustive utilization of local minimization, and 2) the discovered structures of local minima, used as initial conditions to the comparison and selection of new structures to be minimized. Among these methods, the Basin-Hopping [5,6] and the Genetic Algorithm (GA)[7] have been the most promising [5, 6, 8, 9], incorporating the two above-mentioned instruments. Within this work, we will focus on the applications of GA in the research of nanoalloys of Al and Na. In traditional non-biased methods, such as the Monte Carlo and the Molecular Dynamics Simulated Annealing approaches, the difficulties on finding the global minima (GMs) remain[10, 11].

The interest in the research of metal clusters arises mostly from the possibility of creating new alloys from materials in nanoscale, the so-called "nanoalloys". The theoretical research of nanoalloys has an important role in materials science, and some of its most relevant objectives are: the prediction of stability in structures, their growth, and assistance in the interpretation of spectroscopic and other experimental measures. In this context, it should be highlighted that a great number of methods were reported in the last few years regarding the effective global optimization of atomic and molecular systems.

Methodology

Inspired by Darwin's theory of evolution by natural selection, the genetic algorithms (GA) concern the field of artificial intelligence, and, more specifically, evolutionary computation. It consists in a technique that solves a problem by using an evolutionary process where the surviving solution is, consequently, the best adapted, i. e., developed.

We may compare the GA method with the cells of a living organism – DNA blocks – located in specific positions and components of the same group of chromosomes. These blocks codify certain proteins as well as a given feature of the organism, such as skin color. The parental gene pool crossover is to combine during the reproductive process, resulting in a new chromosome that may mutate due to alterations in the DNA, which are usually caused by some factors such as failure in the copies from the parental gene pool. Biologically formed, the offspring adapts or not to its environment, where survival is a measure to its adaptation[12]. The mathematical modeling of this analogy consists in the application of the GA technique to the resolution of a problem by searching a solution that may come up among a variety of other possible solutions and be considered the best option, according to the marking of possible solutions in conformity with its adequacy to the intended answer. In this context, the GA have often been employed in the determination of maxima to the adequacy values regarding the potential energy surfaces associated to the cluster structure[13,14]. Once the GA standard method is applied, the use of evolutionary genetic operators (OP) becomes quite common, bearing resemblance to the crossover operators among individuals (also known as the mating operator), as well as to the Mutation and Natural Selection operators, used towards a test population with the purpose of optimizing, for instance, the cluster structure. The determination of the best-adapted individuals depends on the "quality" assessment, i. e., on the adequacy of each individual that contributes to the system. In the GA model, such assessment is obtained according to the Fitness Function (FF)[15] that, in the context of the clusters, is used to assess the respective energies.

The solutions found in the use of the observed technique (GA) are usually considered adequate, since it is not always possible to find or prove which solution is optimal. The GA used in this research has two other evolutionary operators that distinguish them from the standard GA: the Annihilator (AN) and the History (H)[16,17].

Considering the composition and size of the cluster (total amount of atoms), its population is generated at random, given that the spatial coordinates from each atom in each cluster are generated at random inside a search space previously defined. After this stage, the GA method uses a list of atomic Cartesian coordinates from each cluster, with the purpose of generating their respective genes, which evolve to the next generation by the application of genetic evolutionary operators from the standard method of Crossover, Mutation and Natural Selection. In this context, the genetic operators are applied to the current population, immediately after each individual of this population is relocated to its nearest local minimum according to the quasi-Newtonian standard method (BFGS) [18].

In the current research, the parental individuals are chosen to the application of the Crossover OP through the roulette-wheel selection method. Therefore, the probability of a choice depends on the adequacy of the individual. Once this process occurs, the use of the Mutation OP may or may not be put into effect, considering that this operator is slow and less frequent, so that its application may occur strictly to a fraction of a population from each generation. This does in no way differ from the GA standard method, and yet, in the Mutation OP, the AN removes both offspring individuals and mutants yielding the same energy when compared to already existent individuals from the same generation, while H "memorizes" information concerning the population of that generation for a next use. Hence, the remaining individuals are classified in a list and arranged according to their FF values, where the last-placed in the list are discarded, so it may persist with a constant number of clusters within the population (Natural Selection)[19].

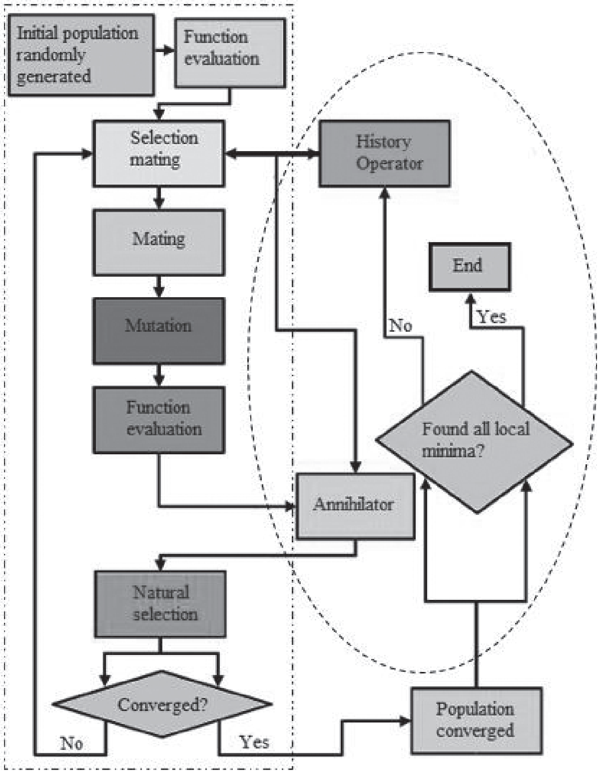

Figure 1: Flow chart indicating the operation of the GA used in this research. The traced box on the left corresponds to the operators of the standard method, while the traced ellipsis to the right indicates the new operators.

The described procedure is a loop from the standard GA (except for a minor interference of AN and H) and is repeated in a determined number of times until convergence, in which it is not possible to produce any more energy. To the GA, henceforth, the global minimum has been found. However, since it is a stochastic process, it is possible that the true global minimum may not be found. For this reason, the better improvement of the modified GA in this research lies in the realization of new cycles, starting from the point where the AN promotes a mass extinction of the system optimized by the standard method. In this case, the procedure reboots and the initial population is no longer generated at random, but provided by H. This new complete loop may now be repeated until, after a determined number of times, no isomer with energy lower than the last more stable obtained is found [17].

Thus, considering the basic functioning of the GA, it is pointless to target a problem regarding clusters with overly strict ab initio treatments, such as the DFT method (Density Functional Theory), due to the great quantity of local minimizations that the optimization algorithm is supposed to perform. For this reason, an analytical description, experimentally parameterized to the potential energy among the atoms of the system (demanding much simpler computational requirements), is the most reasonable option. Expressions used in potential energy associated to a many-body system are denominated "empirical many-body potentials", widely recognized for being capable of modeling in close approximation the bonds between metal atoms, as well as of reproducing accurately the thermodynamic and structural properties, mainly from most of the transition metals[17,20].

Currently, it is recognized that the empirical many-body potential energy expressions are capable of reproducing thermodynamic and structural properties of many transition metals with good accuracy, such as the energy of sublimation, the constant of network, elastic constants and vacancy formation energy[21,22]. This is, to the date, one of the most practical manners of addressing simulations of punctual or extended defects, as much as interface or surface properties in metal alloys [16]. Thus, in the last few years, there has been frequent use of empirical potentials towards the analysis of several problems, in the example of the materials science.

The empirical many-body potential energy expressions present a superior efficiency when compared to simpler potential expressions that only add contributions due to pair interaction, from which the latter is usually the most adequate in the reproduction of basic features of metal systems. This occurs because in the former it is included the essential feature of band regarding metal alloys [20]. Such expressions concern the effect of each individual (j) from the system in reference to one of the components (i) of the same system, not inasmuch as it depends solely on the interaction of each pair (ij), but considering also the influence in which the neighbors, so far as to a certain distance from each individual in question (j), exert on the caused effect in the assessed component (i). We must highlight that all these contributions are added to all existent i and j in the system.

We have it that the Gupta potential belongs to a class of pair-functional potentials based on the Tight-Binding Second-Moment Model. The Gupta potential may be written in the manner of repulsive pairs Vr and term of many-body coupling Vm. The energy of a given atom i constituted by the interaction with all the neighboring atoms j is, accordingly:

$$Vclus = \sum_{i}^{n} \left(Vr(n) - Vm(n)\right) \qquad \textbf{01}$$

where Vr represents pair repulsion among metal ions, and is given by:

$$Vr(n) = \sum_{i}^{n} Aexp\left(-p\left(\frac{rij}{r0} - 1\right)\right) \qquad \textbf{02}$$

Subsequently, the many-body term, Vm, represents the cohesion of many bodies given by the valence band, i. e.,

$$V_m(n) = \left[\sum_{i}^{n} \zeta exp\left(-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right)\right]^{\frac{1}{2}} \qquad \textbf{03}$$

The parameters A, p, r0, ζ e q are values obtained from adjustments in experimental data of the cohesion energy, parameters of network and elastic constants, independent of the crystalline structure at 0 K, not only to pure metals but also to alloys. The term rij is the distance between atoms i and j; the parameters q and p are dimensionless and determine the extent of the terms of band and repulsion, respectively; whereas A and ζ have energy units and establish the force of these terms. The term r0 is the average distance to the atom's nearest neighbors in the bulk of the metal [23].

The parameters to homodiatomic interactions (Al-Al, Na-Na) within this research were obtained from the literature [24,25]. Simple arithmetic means were used in order to address the heterodiatomic interactions (Al-Na) [23]. In this context, the Gupta potential may be used to model an extensive diversity of solids and clusters, as well as of some alloys.

At Table 1 we present the values of the parameters used in this research.

Table 1: Empirical parameters of the Gupta potential to the system Al-Na

	r0 (Å)	ζ (eV)	p	q	A (eV)
Al-Al	2,8637	1,316	8,612	2,516	0,1221
Na- Na	3,6989	0,2911	10,13	1,30	0,01596
Al-Na	3,2818	0,8035	9,371	1,90	0,06903

The average bond energy is an important quantity that may be associated to the clusters and defined as [16]:

$$E_b = \frac{-V_{clus}(N)}{N} \qquad \textbf{04}$$

The value of Eb must be asymptotically close to the value of the cohesion energy of the bulk related to the atoms that compose the cluster, in the case the clusters are relatively sizable [16].

The second difference of average bond energy among clusters is also a useful quantity to the analyzed structures [26,27]. Its calculation may be performed by the following equation:

$$\Delta_2 E_b(\mathrm{N}) = 2E_b(\mathrm{N}) - E_b(\mathrm{N-1}) - E_b(\mathrm{N+1}) \qquad \mathbf{05}$$

Through this expression, it becomes possible to assess the energetic behavior of a cluster of N atoms in reference to its “neighbors”, i. e., a cluster of N + 1 and another of N – 1. Hence, we may observe stability peaks when $\Delta_2E_b(N) > 0$ or instability when $\Delta_2E_b(N) < 0$.[16]

In spite of being a useful quantity, the efficiency of the second energy difference may be, in some fashion, unreliable, since the stability comparison occurs only to the neighboring clusters. For instance: there might be cases where neighboring clusters may present a very high energetic instability, leading to the demonstration of a stability peak by the cluster of N atoms, not because the structure is stable, but otherwise, because the neighboring clusters were too unstable.

In order to analyze the alloy clusters, the excessive energy provides another useful quantity, which may give information regarding the likelihood of the alloy formation in relation to the formation of the corresponding pure cluster [28,29.] In our approach, the excessive energy of an agglomeration of N atoms in a AlxNaN-x alloy is given by:

$$E_{exc}(A_xB_{N-x}) =$$

$$V_{clus}(A_xB_{N-x}) - x\frac{V_{clus}(A_N)}{N} - (N-x)\frac{V_{clus}(B_N)}{N} \qquad \mathbf{06}$$

Negative values to Eexc (AxBN-x) favor the formation of the corresponding nanoalloy. In this research, we performed the calculation of the excessive energy to all combinations of Al_xNaN_{-x} where $3 \leq N \leq 55$.

Results and Discussions

The results obtained regarding the geometries of pure aluminum (Figure 2) and pure sodium (Figure 3) clusters were analogue, and agree with the literature [25,30] concerning systems of this type, where, however, other methods were utilized to deal with the issue.

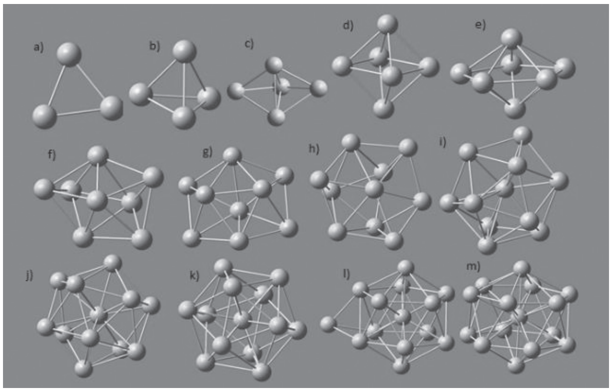

Figure 2: Structures obtained as global minima using the GA regarding pure Aluminum clusters from: a) Al_3 to m) Al_{15}.

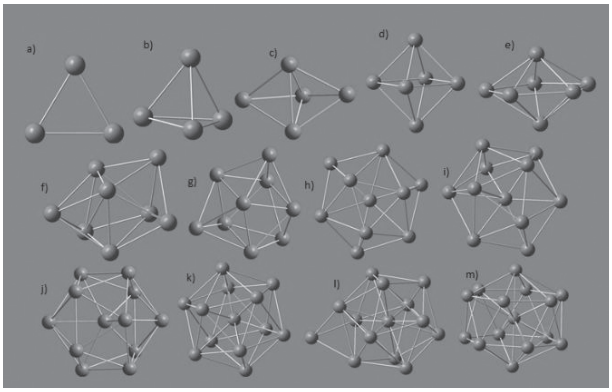

Figura 3: Structures obtained as global minima using the GA regarding pure Sodium clusters from: a) Na_3 to m) Na_{15}.

The pure aluminum structures present sturdier atom compaction if compared to those of sodium. This may be explained by the differences in the atomic radius between those two elements, which are reflected in the equilibrium of interatomic distances provided by the Gupta potential to distinguished atoms. We have verified that the structures of the pure Al clusters are quite similar to those of pure Na, whereas the most important difference occurs in the clusters of 9 and 11 atoms. We noticed that the dihedral angle in the sodium clusters is sharper when compared to the aluminum clusters. Once we compared the structures obtained by the GA using the many-body Gupta potential to the pure aluminum with recent results from the literature, such as those from

Kiohara et al. (2013)[31], we verified that the Gupta potential, despite being a classic method, presented the cluster structure to the systems $\mathrm{Al_2}$, $\mathrm{Al_3}$, $\mathrm{Al_6}$, $\mathrm{Al_8}$ and $\mathrm{Al_9}$ with striking resemblance to those obtained via ab initio calculations, such as DFT and CCSD(T). Since we did not find aluminum doped with sodium clusters in the literature, we managed to provide a few assumptions and observations concerning the behavior of their structures from the analysis of pure sodium and pure aluminum clusters. The following figures present some results to the second energy difference of the clusters $\mathrm{Al_xNa_y}$ regarding different nuclearities.

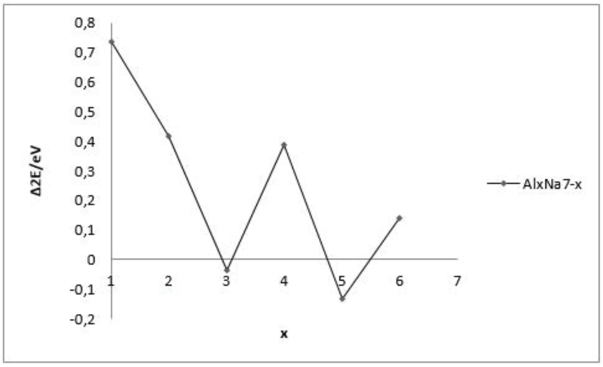

Figure 4: Second energy difference of the clusters aluminum-sodium of 7 atoms.

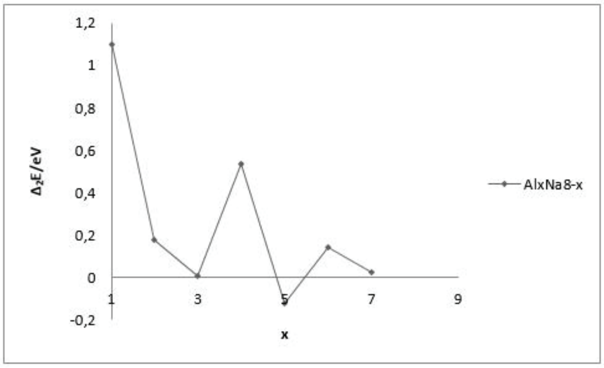

Figure 5: Second energy difference of the clusters aluminum-sodium of 8 atoms.

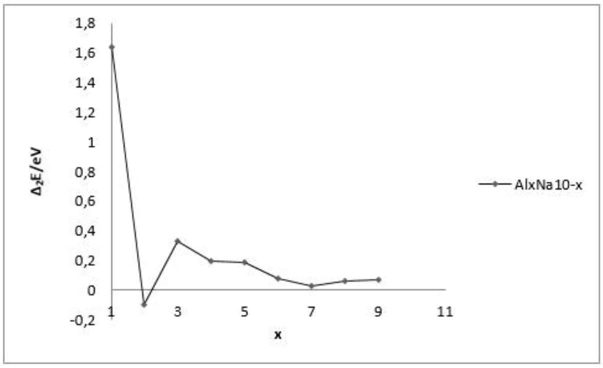

Figure 6: Second energy difference of the clusters aluminum-sodium of 10 atoms.

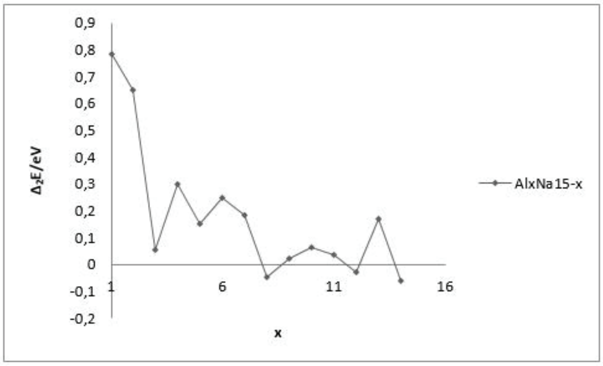

Figure 7: Second energy difference of the clusters aluminum-sodium of 15 atoms.

By performing an analysis of the second energy difference to the aluminum-sodium mixtures, we verified that higher stability peaks occurred with a value of x=1, i. e., when we had but a single atom of aluminum in the cluster structure. However, considering a more detailed analysis of the clusters in an alloy, the excessive energy may become a useful quantity, because it provides the likelihood of the bimetallic alloy formation, when compared to the pure corresponding cluster [28,29]. Next, we present the results from the excessive energies (Eexc) concerning varying compositions of clusters of $\mathrm{Al_xNaN_{-X}}$ $(3\leq N \leq 55)$.

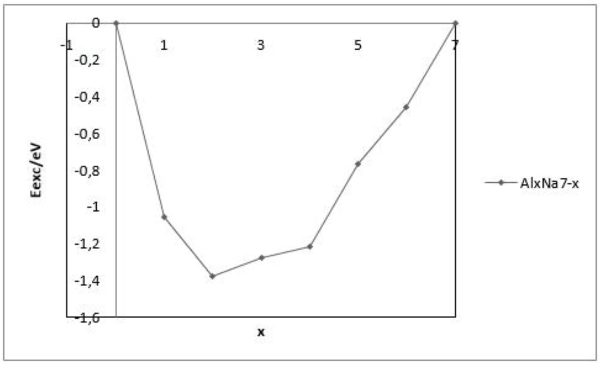

Figure 8: Excessive energy to aluminum-sodium clusters of 7 atoms.

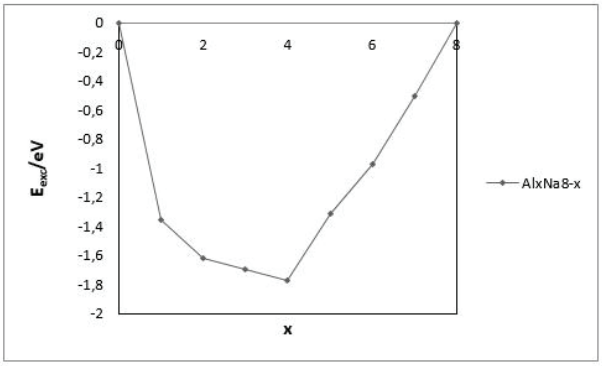

Figure 9: Excessive energy to aluminum-sodium clusters of 8 atoms.

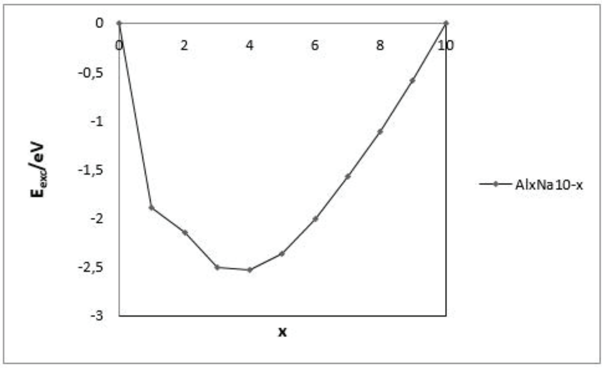

Figure 10: Excessive energy to aluminum-sodium clusters of 10 atoms.

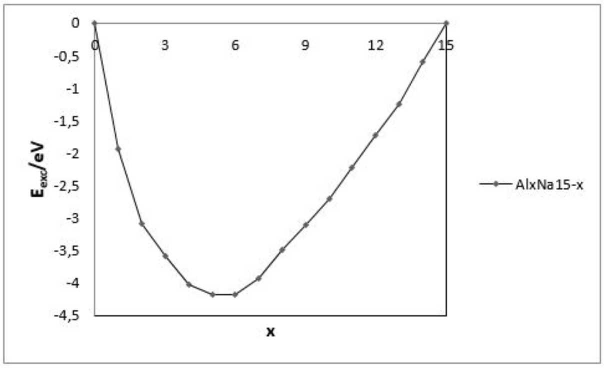

Figure 11: Excessive energy to aluminum-sodium clusters of 15 atoms.

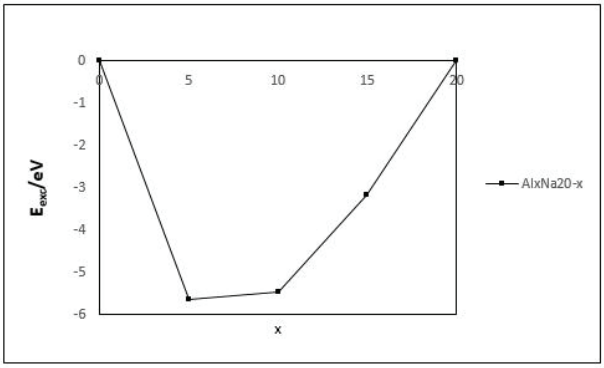

Figure 12: Excessive energy to aluminum-sodium clusters of 20 atoms.

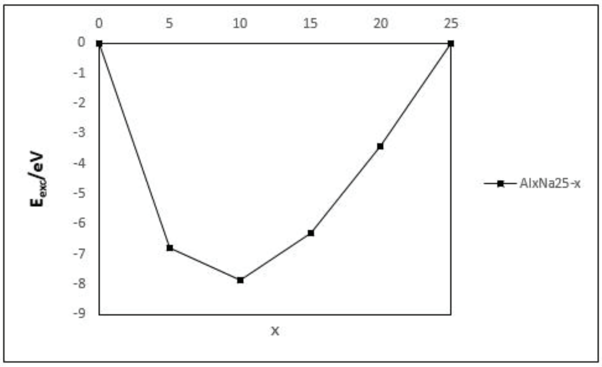

Figure 13: Excessive energy to aluminum-sodium clusters of 25 atoms.

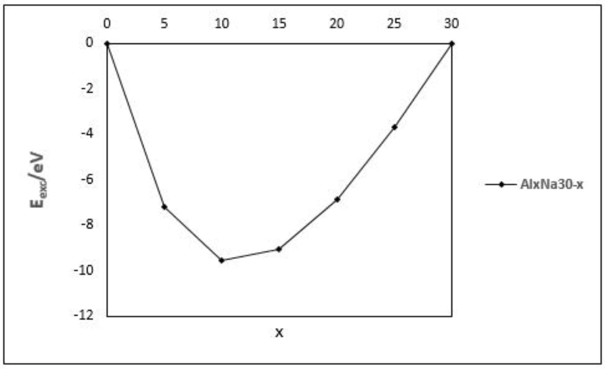

Figure 14: Excessive energy to aluminum-sodium clusters of 30 atoms.

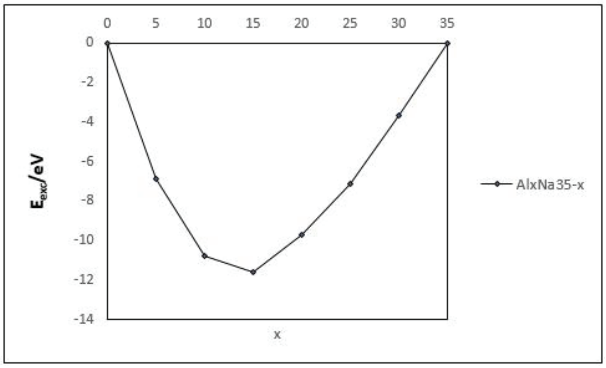

Figure 15: Excessive energy to aluminum-sodium clusters of 35 atoms.

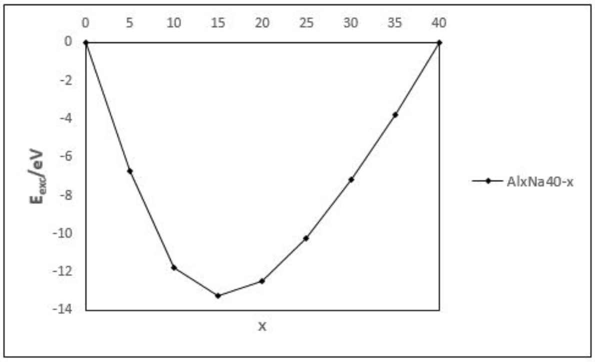

Figure 16: Excessive energy to aluminum-sodium clusters of 40 atoms.

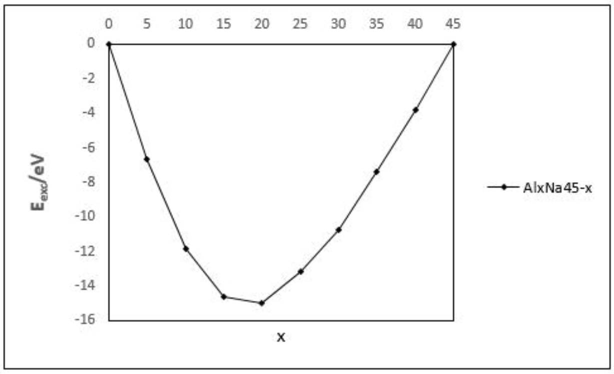

Figure 17: Excessive energy to aluminum-sodium clusters of 45 atoms.

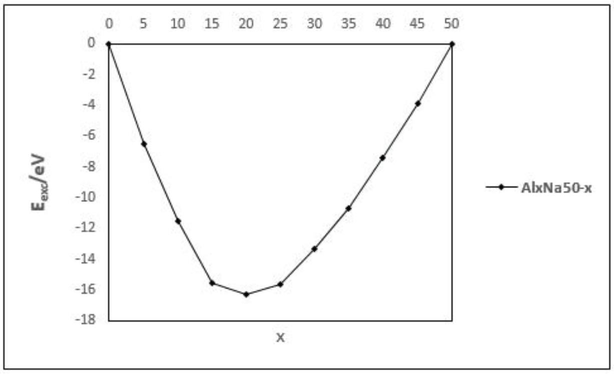

Figure 18: Excessive energy to aluminum-sodium clusters of 50 atoms.

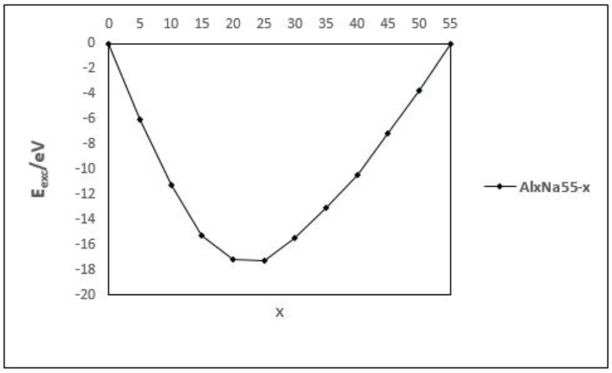

Figure 19: Excessive energy to aluminum-sodium clusters of 55 atoms.

By analyzing the excessive energy graphics, we observe that clusters with 3, 4, 5, 6 and 7 atoms have better stability when the agglomerations are composed of 2 aluminum atoms; in other words, the structures Al_2Na_1, Al_2Na_2, Al_2Na_3, Al_2Na_4, Al_2Na_5 are the ones most prone to be formed. When, considering the structures of nuclearities 8, 9, 10, 11, 12 and 13, the composition is altered and then presents stronger trend to form clusters with the composition of 4 aluminum atoms - Al_4Na_4, Al_4Na_5, Al_4Na_6, Al_4Na_7, Al_4Na_8 and Al_4Na_9. Regarding agglomerations of 14 atoms, the most stable structure was Al_6Na_8, and, to those of 15 atoms, the most stable composition was Al_5Na_{10}. To clusters of 20 atoms, the most stable structure presented 1 aluminum atom. Clusters with nuclearity of 25 and 30 presented better stability with 2 atoms of aluminum in the structure. Agglomerations of 35 and 40 atoms presented better stability with 3 aluminum atoms. Finally, structures of 45, 50 and 55 atoms presented themselves more stable with 4 aluminum atoms in the structure of the nanoalloy. In Figure 20 we present alloy structures with nuclearity up to 15 atoms.

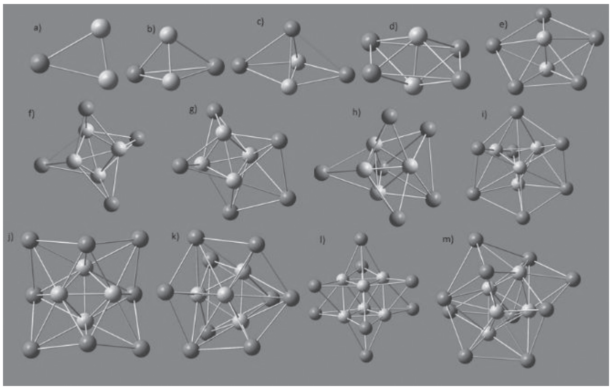

Figure 20: Structure of the compositions Al_2Na_1, Al_2Na_2, Al_2Na_3, Al_2Na_4, Al_2Na_5,Al_4Na_4, Al_4Na5, Al_4Na_6, Al_4Na_7, Al_4Na_8, Al_4Na_9, Al_6Na_8 and Al_5Na_{10}.

We have observed that, regarding sodium structures doped with a single atom of aluminum, the aluminum atoms tend to occupy central positions, whilst sodium atoms tend to occupy peripheral areas within the structure. It is compelling to notice that there is an ordered growth in the structure to the compositions of 4 aluminum atoms (20-f, 20-g, 20-h, 20-i, 20-j and 20-k), in which these atoms form a regular tetrahedron in the center and the sodium atoms agglomerate around those of aluminum, in a very similar fashion to a micelle. We have also verified that the 20-a, 20-b, 20-c, 20-d and 20-e structures presented great similarity to those of pure aluminum and pure sodium with the same nuclearity. With N=8, the structures then started presenting configurations much different from those obtained from pure clusters.

Conclusions

In the current research, all clusters to the system Al_xNaN_{-X} ($3 \leq N \leq 55$) presented structures that may be considered of lesser energy according to the modified genetic algorithm method, along with the many-body Gupta potential [16,17]. We realized that the pure aluminum structures present sturdier atom compaction when compared to those of sodium, which may be explained by the differences in the atomic radius between sodium and aluminum.

Such differences are observed in the equilibrium of interatomic distances provided by the Gupta potential to distinct atoms. Since there is no further research in the literature regarding aluminum-sodium clusters, we started from the obtained structures of pure aluminum and pure sodium in order to predict information regarding to corresponding nanoalloys. Once we considered that the aluminum clusters presented more stability than those of sodium, we focused in the use of pure aluminum structures to serve as a comparative basis for the GA method with the Gupta potential. By confronting the obtained structures using the GA with the many-body Gupta potential to pure aluminum, consonant with recent studies in the literature such as those of Kiohara et al. (2013)[31], we have verified that, despite being a classic method, the Gupta potential presented cluster structures to systems Al_2, Al_3, Al_6, Al_8 and Al_9 in a very similar manner to those obtained from ab initio calculations, such as the DFT and the CCSD(T).

In conformity with what has been explained, it became possible to demonstrate that the genetic algorithms applied to the Gupta potential may be an effective tool in the search for global minima structures.

Acknowledgments

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