Modeling of atomic clusters using evolutionary algorithms.

Artur Stasikowski[1] and Tomasz Gwizdałła[2]

[1] Dept. of Solid State Physics, University of Łódź,
Pomorska 149/153, 90-236 Łódź, Poland, e-mail: a.s@poczta.fm
[2 1] Dept. of Solid State Physics, University of Łódź,
Pomorska 149/153, 90-236 Łódź, Poland, e-mail: tomgwizd@uni.lodz.pl

Abstract. In the paper there is presented a process of preparation of a tool to geometrical optimization of their total binding energy as well as some physical results. Initially the evolutionary algorithm (EA) was responsible for study of metal clusters described by three-body potential. Afterwards the algorithm was used to perform the exact investigations or rare gas clusters and their modifications by the alkali metal ion doping. The data presented here are the part of PhD dissertation accepted by the Faculty of Physics UŁ [1] where are detailed information can be found.

1 Introduction

Atomic clusters are isolated systems of atoms containing from several to even thousands atoms. They are intermediate phase between single atom and condensed matter. Thus, because of small sizes, clusters are visibly different from bulk material and create a new form of matter showing some elements of symmetry similar to symmetry in bulk systems. For this reason the interest in these systems rises all the time. The main goal of this research is to find the realization of atomic and electron structures and their characteristics which associate the process of cluster growth. This knowledge helps to understand the mechanism of atomic clusters creation and to find new molecules [2]. From theoretical point of view geometrical modeling of atomic clusters consists of finding the atoms arrangement with global minimum (GM) total binding energy which can be found on PES, an 3N hypersurface in 3N+1 dimensional space, where N is the number of atoms. The determination of total energy could be realized by *ab initio* molecular theory (like density functional or Hartree-Fock method), molecular dynamics, or analysis of two and three-body potentials describing atomic interactions.

The task of minimizing of energy of atomic structures is very difficult because potential energy surface (PES) has many deep and short peaks and except of this, the number of local structures increases exponentially with the increase of cluster size (one approximates this dependence $\exp(0{,}36N+0{,}03N^2)$). Because of that reason finding global minima becomes not trivial (NP-hard) problem especially for quite large systems. There are three the most popular and the most efficient methods of GO which are used to model atomic clusters: basin-hopping algorithm [3] (which uses energy minimization and Monte-Carlo simulation), conformational space annealing [4] (which is extension of simulated annealing) and evolutionary algorithms [5] which are one of the methods of artificial intelligence and which we used into our work.

2 Method and tests

Let us start from the definition of the form of evolutionary operators. First problem is the choice of the suitable fitness function. In our problem we selected fitness function in exponential form [6]:

$$f(V) = e^{-b\frac{V-V_{\min}}{V_{\max}-V_{\min}}}, \tag{1}$$

where: V - is binding energy of cluster, V_{min} and V_{max} are the lowest and the highest total energy in population, and parameter b - determines the selectivity of the fitness function (b=1 in our work). The simplest way to determine binding energy of N-atomic system is to calculate the sum of two-body interaction energies

$$V = \sum_{i}^{N-1}\sum_{j>i}^{N}\varphi(r_{ij}). \tag{2}$$

We selected two-body Lennard-Jones(L-J) [7] potential which was created to describe interaction between atoms of noble gas. This potential has sharp shape of its function, for this reason is highly selective for different algorithms and works as is very popular benchmark for methods of optimization.

$$\varphi(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right), \tag{3}$$

where: ε - is the depth of the potential energy minimum and $\sigma*2^{1/6}$ - is the equilibrium pair separation (in this part of work ε=1, σ=1) .

In previous work [6] we carried out test of efficiency of elementary genetic algorithm in atomic systems described by L-J potential. The system of six atoms has been chosen to the tests, each atom described by three cartesian coordinates, so our EA optimizes 18-parameter function, and make evolution process on 20 individuals during 10000 generation.. The optimal cluster for used potential has octahedron structure. EA reaches global minimum in almost 4,6 % of independent runs. In other cases calculations stop at the local value of energy corresponding to atom arrangement in bicapped tetrahedron. This problem is connected with the shape of L-J potential. Mentioned above sharpness of L-J function is the reason for existence of a lot of local minima. At this point we deal with the so-called deceptive problem, that means premature convergence to local minimum. We used a few modifications in genetic algorithm to overcome this problem [8]. We scaled the fitness function (linear scaling and power law scaling), introduced samples mechanisms in operator of reproduction by changing selection (selection with artificial scales and tournament selection), we modified crossing (two-point and uniform crossover) and mutation operator (non-uniform mutation). We also applied niche and species in our EA.

After many tests of modified EA where carried out we observed higher efficiency in comparison to initial, elementary form of EA [8]. After appropriate combining of different modifications we obtained significant increase of efficiency over 10%.

We also added methods which are based on the knowledge of the problem. In this case it could be sorting of coordinates in each clusters in crossover operation. Sorting operation is based on arranging the elements of code sequence (coordinate of the position of atoms) according to one of the coordinates in the space of solution. We also used rotation of clusters according to 3 random Euler angles. This operator is used in relation to one individual from each pair taking part in crossing. Sorting as well as rotation combined with the previous genetic algorithm modifications increase efficiency of finding global minima even up to 50%.

We also used the local optimization in evolutionary process to improvement the efficiency of our algorithm. Many tests carry out which show that the global optimum may be found in the earlier generations and in evolutionary modeling of atomic clusters the use of local optimization to the all individuals in population is the most effective way.

Combining local optimization with suitable methods of evolutionary modification gives possibility to obtain global minima of six atomic cluster after a few more 4 generations.

3 The modeling of real materials described by three-body potentials

The next step was to use our improved evolutionary algorithm to the real materials for which the three-body potential parameters are known. One can expect that such a potentials would better describe the properties of real materials because except of direct two-body interaction they take into account also the influence of neighborhood what can be understand as a form of molecular field. Due to its complex character we will not present here their strict, mathematical form.

3.1 Mottram-Murrell potential for metal clusters

The Mottram-Murrell potential is the three-body one composed generally from two parts. The first one is the classical two-body Rydberg interaction energy function. The second one comes from the group theory investigations and has a polynomial form. So far the Mottram-Murrell potential has been used to study some dynamical properties of different solids (from alkali metals, rare earth, and transition metals up to intrinsic semiconductors or lanthanides) for which the parameters was fitted on the base of experimental data [9].

In consequence of cluster optimization for few cluster sizes N we obtained close and high-symmetry structures *Al*, *Ag*, *Au* as is illustrated in Figure 1, which correspond to the value of energy in global minimum [10]. These structures are consistent with two-body modeling systems which ware received by other groups [11].

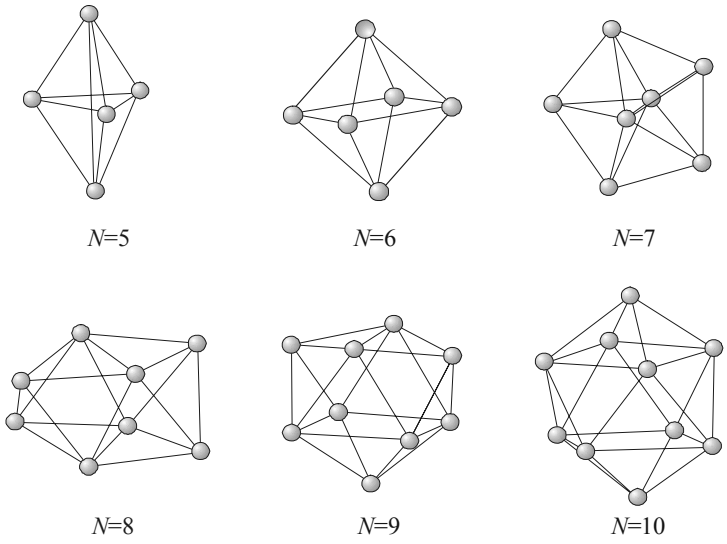

Figure 1. The clusters of Al, Ag and Au.

3.2 Brenner potential for carbon

The Brenner [12] potential is sometimes called the geometrical one, because the influence of third atom is considered by same trigometrical formulas.

In consequence of cluster C_N optimization for few cluster size (N) we obtained chain (N=4,5) and ring structures (N=6,7,8), for bigger clusters size (N>10) there are cage structures (Figure 2).

Forms of structures received are comparable with results of molecular dynamics [13].

Genetic algorithm was also used for optimization of large structures like fullerene C_{60}, where atoms were represented by spherical coordinates. This kind of representation required reconstruction of some evolutionary operators.

In case of fullerene C_{60} (Figure 3) value of total energy system was different from global value of system only by several percent.

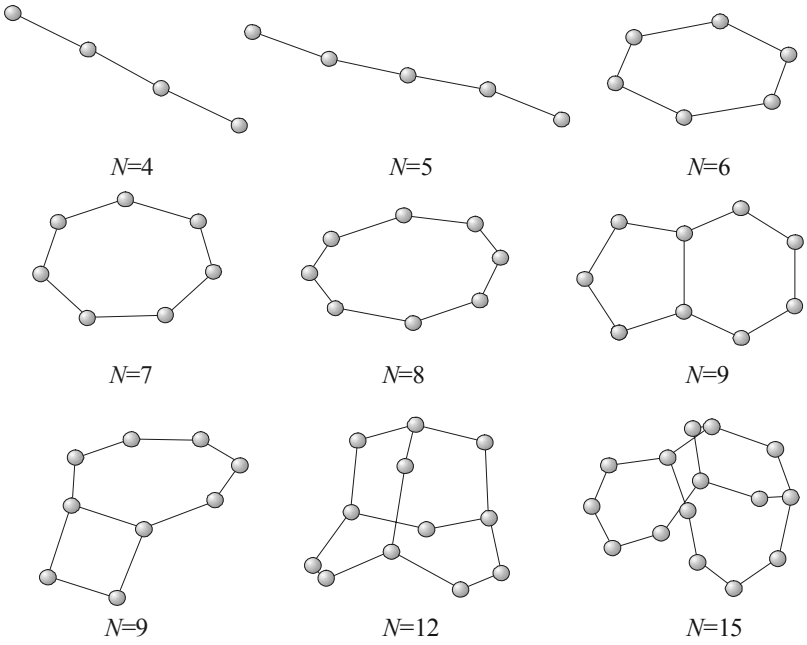

Figure 2. The clusters of carbon for Brenner potential.

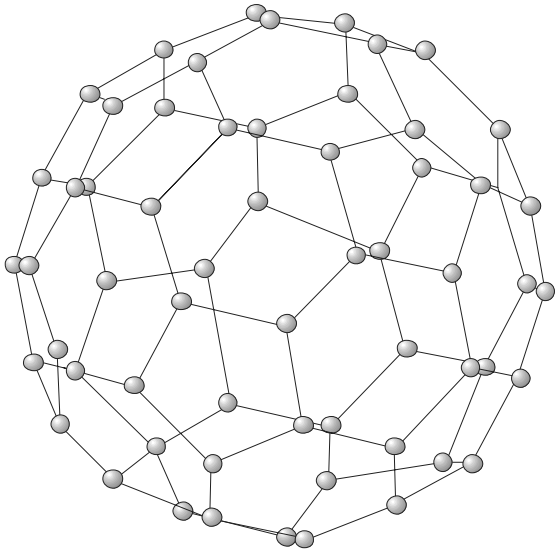

Figure 3. Calculated structure of fulleren C_{60}.

4 The alkali metal atoms doped noble gas clusters

As it has been presented the task of structure optimization according to the total interaction energy minimization is relatively popular problem but solved for different monoatomic clusters. In this part we want to show the results obtained with the global optimization method of evolutionary algorithm applied to the noble gas clusters doped with single alkali metal atom.

In this systems the main questions is how structural and electron properties change replacing one of the noble gas atoms with the metallic one. They were certainly inspired by some experimental results showing the changes of magic number values or mass spectra following the substantial structure change.

In order to calculate of noble gas clusters total energy doped with metallic atom we have to describe mathematically two types of interactions: the first one between two noble gas atoms (G-G) and the second one between the gas and metal atoms (G-M),

$$V = \sum_{i=1}^{N-1} \sum_{j>i}^{N} \varphi\left(r_{ij}\right)^{G-G} + \sum_{j=1}^{N} \varphi\left(r_{0j}\right)^{G-M} . \tag{5}$$

For both cases we use the typical selection of two-body potential. For gas atoms interaction the well known Lennard-Jones function is used (3). The G-M interaction is described by the similar function proposed by Mason and Schamp [14]:

$$\varphi\left(r_{ij}\right) = \frac{\varepsilon_{MS}}{2}\left((1+\gamma)\left(\frac{\sigma_{MS}}{r_{ij}}\right)^{12} - 4\gamma\left(\frac{\sigma_{MS}}{r_{ij}}\right)^{6} - 3(1-\gamma)\left(\frac{\sigma_{MS}}{r_{ij}}\right)^{4}\right). \tag{6}$$

The additional factor r^{-4} has a sense of electrostatic interaction between the alkali ion and the induced dipole moment of inert gas atom, so γ may be understood as a weighting multiplier determining the significance of this electrostatic force as compared to the dispersion one. It takes the values from the period [0,1] and doesn't influence the equilibrium distance which is equal to σ_{MS}. Analogically to the L-J potential also here ε_{MS} corresponds to the minimum energy. The Mason-Schamp potential has been introduced in order to study the kinetics of atom passing through the gaseous medium and such a studies are still the main source of its parameters data [14]. Table 1 presents real values of both two-body potentials. It can be noticed that although the separation values are similar, the G-M interaction is about 12 times stronger than G-G.

Table 1. Typical values of parameters for Lennard-Jones and Mason-Schamp interaction potentials.

interaction	ε_{LJ}**[eV]**	$\sigma_{LJ}*2^{1/6}$ **[Å]**	ε_{MS}**[eV]**	σ_{MS}**[Å]**
Ar - Ar	0,01	3,82		
K^+ - Ar			0,121	3,0

Evolutionary algorithm allowed us to model pure al well as potassium doped argon clusters in the wide range of sizes from N=3 to N=60 the doping causes structural changes just from N=5, from N≥7 so called caging may be observed. It means that the alkali metal ion is located inside

the “box” build of gas atoms. For smaller clusters alkali metal ion is at the surface. The introduction of impurity causes also distinct changes of magic numbers what show as peaks on Figure 4 which visualizes the value of second energy difference:

$$\Delta_2 V(N) = V(N+1) + V(N-1) - 2V(N). \tag{7}$$

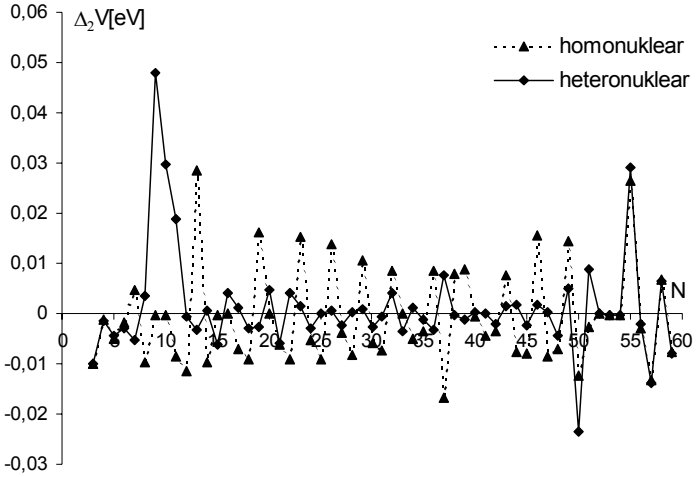

Figure 4. Magic numbers of pure doped with ion potassium argon clusters.

Change of magic number takes a stand in cluster range from 3 for 49 atoms. Influence is low above size on 49 atoms predominating interaction atom -ion so much that they return to typical for rare gas structures of Mackay icosahedron [15].

The dependence of energy per atom on cluster size is shown on Figure 5 where curves reflects the behaviour of experimental data. In the case of pure rare gas clusters, along with the grow of cluster size also the temperature of dissociation grows up. The rare gas cluster doped with metal ion the dissociation temperature grows only to N=9 atoms, then it starts to decrease what is connected with observed screening caging effect [16].

System of closest neighbours was one of the four the same structures (N=9, 10, 11, 13) after add up another atoms. Kind of these structures had an influence on value of total energy and cluster symmetry thus the next part of computation was devoted to the search of new structures by change of relation between binding coefficient (G-G/G-M). This makes possible to create a two-dimensional phase diagram showing which type of structure corresponds to the minimum energy for the selected pair of multipliers. These results were shown in our previous work [17].

5 Conclusions

The application of global optimization methods in physics is very interesting for a few reasons. First of all a lot of physical problems is computationally hard to solve in an analytical way. For such a class of questions the heuristic attempt may be a sensible offer. It concerns especially multimodal problems where we deal with a lot of local solutions which can lead to the erroneous results. It exists also a set of simulational algorithms (like some magnetic ones) which must start

from the global energy minimum. From the other hand physics offer possibilities to create a tests checking the efficiency of designed optimization algorithms.

Global optimization will not replace the experiment and concrete physical theory because it almost always follows in their shadow being one step behind in explaining the recognized problems but one step ahead in the expectations because these method is fast and cheap.

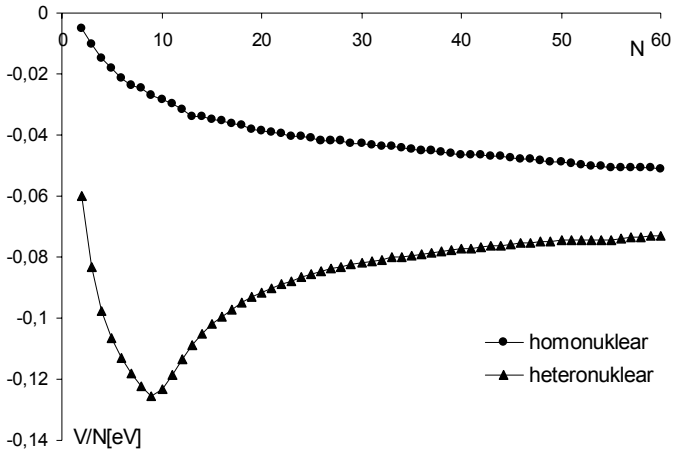

Figure 5. Energy per atom in the function of cluster size.

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