Global minima of Al\(_N\), Au\(_N\) and Pt\(_N\), \(N \leq 80\), clusters described by the Voter–Chen version of embedded-atom potentials

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Abstract

We report the global minima for aluminium, gold and platinum metal clusters modelled by the Voter–Chen version of the embedded-atom model potential containing up to 80 atoms using the basin-hopping Monte Carlo minimization approach. The results show that the global minima of the Al, Au and Pt clusters have structures based on either octahedral, decahedral, icosahedral or a mixture of decahedral and icosahedral packing. The 54-atom icosahedron without a central atom is found to be more stable than the 55-atom complete icosahedron for all of the elements considered in this work. Most of the Al global minima are identified as face-centred cubic structures and many of the Au global minima are found to be low symmetric structures, both of which are in agreement with the previous theoretical and experimental studies. Although many of the Pt global minima are identical with the global minima of the corresponding Au clusters, the most stable sizes of the Pt clusters correspond to the same sizes of the Al clusters.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The use of metal and semiconductor clusters as components of nanodevices is one of the most important reasons for the considerable theoretical and experimental interest in the study of gas phase and supported metal clusters within the last several decades [1–5]. Owing to their finite size, these small particles may have totally different structures and material properties from their bulk crystalline forms. Furthermore, these properties may sometimes change drastically whenever a single atom is added to or removed from the cluster [6]. A systematic study of evolution of these properties with size allows elucidation of the transition from the molecular
structure to their condensed matter phases. Clusters, in particular metal clusters, play an important role in many chemical reactions as catalysts as well. Structures of the small metal clusters in reactions can have a major effect on the rate of formation of the products [7], and size effect was observed in experiments [8].

In this study, using the basin-hopping [9] Monte Carlo (MC) minimization approach we report the global minima for the aluminium, gold and platinum metal clusters modelled by the Voter–Chen [10, 11] version of the embedded-atom model (EAM) [12] potential containing up to 80 atoms. The virtue of the Voter–Chen potentials is that they are derived by fitting to experimental data of both diatomic molecules and bulk metals simultaneously. Therefore, it may be more appropriate for a wide range of sizes of the clusters since almost all properties of the small clusters are size dependent.

This paper is organized as follows: the interaction potential and the computational procedure are discussed in section 2. Results and discussions are presented in section 3, and conclusions are given in section 4.

2. Computational methods

2.1. The Voter–Chen potential

In any $N$-scaling energy expression total energy, $E$, of a system of $N$ atoms can be written as a sum

$$E = \sum_i E_i. \quad (1)$$

In the EAM, the configuration energy $E_i$ of atom $i$ is represented as

$$E_i = \frac{1}{2} \sum_{j \neq i} \phi_{ij}(r_{ij}) + F_i(\bar{\rho}_i). \quad (2)$$

where $F_i$ is the embedding term, $\phi_{ij}$ is the pairwise-addition part of the interaction between atoms $i$ and $j$, $r_{ij}$ is the distance between atoms $i$ and $j$, and $\bar{\rho}_i$ is the total ‘host’ electron density at the position of atom $i$:

$$\bar{\rho}_i = \sum_{j \neq i} \rho_j(r_{ij}). \quad (3)$$

The sums over neighbouring atoms $j$ are limited by the range of the cut-off for $\phi$ and $\rho$, which is approximately 5 Å for the metals considered in this work. Key to the EAM is the nonlinearity of the function $F(\bar{\rho})$, which provides a many-body contribution to the energy. If $F$ were purely linear, the two terms in equation (2) could be collapsed to give a simple pair potential. The $\bar{\rho}_i$ depends only on scalar distances to neighbouring atoms, therefore, the many-body term has no angular dependence. Nonetheless, this spherically symmetric, many-body term is quite important.

All the parameters in the Voter and Chen model were determined by minimizing the root-mean-square deviation ($\chi_{rms}$) between the calculated and experimental values of three elastic constants ($C_{11}$, $C_{12}$ and $C_{44}$), the unrelaxed vacancy formation energy ($E_{\text{f, vac}}$) of the bulk metals (Al, Au and Pt) and of the bond length ($R_e$) and bond strength ($D_e$) of their diatomic molecules.

2.2. The basin-hopping algorithm

Some new and more successful algorithms have been developed within the last two decades to search for the global minimum of an energy landscape. Two of those methods are basin-hopping and genetic algorithms, which are different from the traditional random search and
simulated annealing techniques. The genetic algorithm is a search based on the principles of natural evolution [13], whereas the basin-hopping approach belongs to the family of hyper-surface deformation methods [14], where the energy landscape is transformed into a smoother surface. The basin-hopping algorithm which we have used in this work is based upon Li and Scheraga’s [17] MC minimization, and it has been developed and employed for several systems by Doye and Wales [9, 15, 16]. In the basin-hopping algorithm, the transformed potential energy surface (PES), \( \tilde{E}(X) \), is defined by \( \tilde{E}(X) = \min\{E(X)\} \), where \( X \) represents the vector of atomic coordinates and \( \min \) signifies that an energy minimization is performed starting from \( X \). Unlike many PES transformations, this basin-hopping transformation guarantees the preservation of the identity of the global minimum. The topography of the transformed surface is that of a multi-dimensional staircase (a set of interpenetrating staircases with plateaus corresponding to the basins of attraction of each minimum). Since the barriers between the local minima are removed in the transformed PES, vibrational motions within the well surrounding a minimum are removed. In addition, transitions from one local minimum to another in the transformed PES can occur at any point along the boundary between these local minima whereas on the untransformed surface these transitions can occur only when the system passes through the transition state. Consequently, on \( \tilde{E}(X) \), the system can hop directly between the basins; hence, it is the name of this transformation.

We have used the GMIN [18] program in our simulations to locate the lowest energy structures of the Al, Au and Pt clusters. The MC runs have been started with the configurations which are the global minima of the Morse clusters. For a given size, as the interaction range of the Morse potential changes, the global minimum varies. Different global minima for different interaction ranges of the Morse potential were reported up to 80-atom clusters before [19, 20]. We have reoptimized all these Morse global minima by performing several MC runs of 100,000 steps for each of them. It should also be mentioned that there are some limitations in all minimization methods, and therefore one cannot always be sure of having explored all the minima. However, we believe that we have located the lowest stable energy structures at least for most of the studied sizes in this work.

3. Results and discussion

3.1. Aluminium clusters

Since the mid-eighties, a number of theoretical studies of Al clusters have been carried out by different groups [21–40]. These studies range from the simple jellium model [21], where cluster geometry is ignored, to a number of models where the geometry enters explicitly into the picture including semiempirical molecular orbital calculations [22], quantum molecular dynamics [27–30, 32], quantum-mechanical calculations based on quantum-chemical [23–25] and density-functional [26–34] theories (DFT) within local density or local spin-density approximations, molecular dynamics and MC simulations based on empirical model potentials [35–40]. The icosahedral form of Al\(_{13}\) in particular has been studied intensively [25, 33]. The most recent and more extensive density-functional calculations have been presented by Ahlrichs and Elliott [30] and by Rao and Jena [34]. These studies focused both on electronic and structural properties of neutral and ionized Al clusters up to 15 atoms, respectively. On the other hand, although the empirical model potential studies [35–40] cannot calculate the electronic properties of the clusters, it is possible to search PES of higher sized clusters with them since they are computationally much less demanding than \textit{ab initio} calculations. In these model potential studies—carried out by random search, simulated annealing or genetic algorithms—the Al clusters are described by an empirical many-body potential [35], two-plus-three body
Murrell–Mottram potential [36–38], Gupta [39] or Sutton–Chen [40] potentials. Here, the works of Lloyd et al. [38] and Joswig and Springborg [40] have been the most extensive. However, Al clusters have been studied up to 55 and 58 atoms in these works, respectively. Our present work extends the size of the clusters to 80 atoms which are investigated in detail. Furthermore, it presents the results obtained using an alternative many-body potential and an alternative method of investigation. On the other hand, experimental studies on the Al clusters [41–52] go back to the mid-eighties. It is known that while the electronic factors determine cluster stability for alkali metal clusters [53], packing and surface energy effects dominate the structure of alkaline earth elements, such as calcium and strontium [52]. Aluminium, however, is placed at a central position between the regimes of electronic and geometric shells [46]. Martin’s mass spectroscopic studies [52] have shown that Al clusters with up to a few hundred atoms have face-centred cubic (fcc) packing structures. These experimental interpretations have been confirmed by theoretical calculations using empirical potentials [39] and DFT [30]. Jarrold et al. [42] have performed experiments on smaller Al clusters which enabled them to determine the topologies of clusters with tens of atoms.

We have reported the total energies ($E$), the point groups (PG) and the structural assignments (SA) (whenever possible) of the global minima for the Al clusters up to 80 atoms described by the Voter–Chen potential in table 1. The PG of the structures are determined with OPTIM program [18]. Symmetry elements are diagnosed when rotation and reflection operators produce the same geometry (correct to 0.001) in each Cartesian coordinate. The energies and the second finite differences in energies

$$D^2E(N) = E(N + 1) + E(N - 1) - 2E(N),$$

are plotted in figures 1(a) and (b), respectively. Following Northby et al. [54] and Lee and Stein [55], the function,

$$E_0 = aN + bN^{2/3} + cN^{1/3} + d,$$

is fitted to the energies given in table 1, and it is subtracted from the energies of the clusters in order to emphasize the size dependence. In this polynomial function, $a$ describes the volume, $b$ surface, $c$ edge and $d$ the vertex contributions to the energy. $D^2E$ is generally correlated with the magic numbers observed in mass spectra. Clusters are particularly abundant at magic number sizes in mass spectra as they are the most stable ones [56].

The triangulated polyhedral structures of the Al$_7$–Al$_{80}$ global minima are illustrated in figure 2. The structures for the first seven Al$_N$ clusters ($N = 2–8$) are similar to those obtained by the other empirical potentials for aluminium [37, 40] and for the other metals [15, 57]. Al$_3$ forms an equilateral triangle, Al$_4$ is a tetrahedron, Al$_5$ is a trigonal bipyramid, Al$_6$ has an octahedral form, Al$_7$ is a pentagonal bipyramid and Al$_8$ is a bicapped octahedron. All of these structures are located as the global minima of the Au and Pt clusters in this work too.

What is important at this point is that since Voter–Chen EAM potentials have been produced by fitting the parameters of both diatomic molecules and the bulk simultaneously, it produces better values for the binding energy and the bond length of the dimers. In the case of Al$_2$, the experimental data [58] are 1.60 eV and 2.47 Å, respectively. The bond length has been calculated as roughly 2.5 Å in the $ab$ initio study of Upton [24]. The corresponding results obtained in this work are 1.54 eV and 2.45 Å, respectively. However, the bond length has been calculated as 2.09 Å in [40] and as 2.76 Å in [37]. No binding energy was reported in [40] and it has been calculated for an Al dimer as 0.90 eV in [37]. Therefore, since most of the similar previous calculations were carried out using some potentials, which have been produced by fitting only to the parameters of the bulk, one could expect that the given binding energies in this work are more reliable than the previous calculations for the small-sized clusters. Al$_9$ can be described as a three-capped trigonal prism and Al$_{10}$ is a hexadecahedron, which are the
Global minima of Al$_N$, Au$_N$ and Pt$_N$ clusters

Table 1. Global minima for Al clusters. For each minimum energy ($E$), PG and SA are given if possible. The structural categories are: centred (cl), ucel and fsl; packed fcc; decahedral with $n$ atoms along the decahedral axis (dec($n$)); involving a mixture of staking sequences (mix).

| $N$ | $E$ (eV) | PG   | SA  | $N$ | $E$ (eV) | PG   | SA  |
|-----|---------|------|-----|-----|---------|------|-----|
| 2   | -1.5443 | D$_{6h}$ | 42  | -113.6500 | C$_{3v}$ | fcc  |
| 3   | -3.7442 | D$_{3h}$ | 43  | -119.5276 | C$_{3v}$ | fcc  |
| 4   | -6.3998 | T$_d$    | 44  | -122.5599 | C$_2$   |     |
| 5   | -8.9663 | D$_{3h}$ | 45  | -125.6996 | C$_{2v}$ | fcc  |
| 6   | -11.8950 | O$_h$  | 46  | -128.5274 | C$_2$   |     |
| 7   | -14.5508 | D$_{3h}$ | 47  | -131.4723 | C$_{2v}$ |     |
| 8   | -17.2960 | D$_{2d}$ | 48  | -134.5603 | C$_2$   |     |
| 9   | -20.0965 | D$_{3h}$ | 49  | -137.4842 | C$_2$   |     |
| 10  | -22.8679 | D$_{4d}$ | 50  | -140.8376 | D$_{3h}$ | fcc  |
| 11  | -25.5008 | C$_{2v}$ | cl  | 51  | -143.7037 | C$_{3v}$ | ucel |
| 12  | -28.5274 | C$_{5v}$ | cl  | 52  | -146.9402 | D$_{2h}$ | fcc  |
| 13  | -32.0279 | I$_h$   | cl  | 53  | -149.9977 | C$_{5v}$ | ucel |
| 14  | -34.4434 | C$_{3v}$ | cl  | 54  | -153.1459 | I$_h$  | ucel |
| 15  | -37.4868 | D$_{5h}$ | 55  | -155.9151 | I$_h$  | cl   |
| 16  | -40.2857 | C$_{2v}$ |     | 56  | -158.6939 | C$_1$ |     |
| 17  | -43.1633 | D$_{4d}$ | mix | 57  | -161.8106 | C$_2$ | fcc  |
| 18  | -45.8783 | C$_{4v}$ | mix | 58  | -164.8037 | C$_{3v}$ |     |
| 19  | -48.8299 | D$_{3h}$ | cl  | 59  | -167.8936 | C$_1$ | fcc  |
| 20  | -51.7096 | D$_{2h}$ | fsl | 60  | -170.8159 | C$_{2v}$ | dec(5)|
| 21  | -54.5367 | C$_2$   | fsl | 61  | -174.1955 | C$_{2v}$ | fcc  |
| 22  | -57.5353 | C$_2$   | fsl | 62  | -176.8996 | C$_2$ | fcc  |
| 23  | -60.4193 | C$_1$   | fsl | 63  | -179.9652 | C$_2$ | fcc  |
| 24  | -63.2273 | C$_1$   | fsl | 64  | -183.1181 | C$_{2v}$ | dec(5)|
| 25  | -66.1897 | C$_1$   | fsl | 65  | -186.0925 | C$_{2v}$ | fcc  |
| 26  | -69.0988 | C$_1$   | fsl | 66  | -189.1802 | C$_2$ | fcc  |
| 27  | -72.0211 | C$_2$   | fsl | 67  | -192.2851 | C$_{2v}$ | dec(5)|
| 28  | -74.9678 | C$_1$   | fsl | 68  | -195.5431 | T$_d$  | fcc  |
| 29  | -77.8530 | C$_1$   | fsl | 69  | -198.2053 | C$_1$ | fcc  |
| 30  | -80.8463 | C$_1$   | fsl | 70  | -201.5432 | C$_2$ | fcc  |
| 31  | -83.9112 | C$_1$   | fsl | 71  | -204.6298 | C$_2$ | fcc  |
| 32  | -86.8113 | C$_2$   | fsl | 72  | -207.4224 | C$_{2v}$ | dec(5)|
| 33  | -89.6630 | C$_1$   | fsl | 73  | -210.6064 | D$_{3h}$ | dec(5)|
| 34  | -92.7060 | C$_1$   | fsl | 74  | -213.7521 | C$_{3v}$ | dec(5)|
| 35  | -95.7977 | D$_{3h}$ | fsl | 75  | -216.9853 | C$_2$ | fcc  |
| 36  | -98.6907 | C$_{2v}$ | fsl | 76  | -219.6910 | C$_4$ | fcc  |
| 37  | -101.6952 | C$_{3v}$ | fcc | 77  | -222.8998 | C$_1$ | fcc  |
| 38  | -105.1156 | O$_h$   | fcc | 78  | -225.9885 | C$_1$ | fcc  |
| 39  | -107.8211 | C$_{4v}$ | fcc | 79  | -229.1335 | D$_{3h}$ | fcc  |
| 40  | -110.5958 | C$_1$   | ucl | 80  | -231.9938 | C$_{2v}$ | fcc  |

same as Joswig and Springborg’s findings [40] for the Al clusters used by the Sutton–Chen potential. Structures of the Al clusters with $N = 11$–14 atoms are icosahedral. The Al$_{15}$ is the sixfold icostetrahedron. The 16- and 17-atom Al clusters involve a mixture of decahedral and icosahedral staking sequences. The Al$_{10}$ is a double icosahedron. In the size range of $N = 20$–36, the Al clusters have face-sharing icosahedral (fsI) structures possessing generally low symmetries. Above the size of 36, most of the Al clusters are fcc packed. This is consistent with Martin’s experimental study [52] with the exceptions of the 40-, 51-, 53- and 54-atom
uncentred icosahedral (uci) structures, the 55-atom centred icosahedron and the 60-, 64-, 67-, 72-, 73- and 74-atom decahedral (dec) structures. As a result, the total number of fcc Al clusters having more than 36 atoms is 26.

It can be seen from both figures 1(a) and (b) that the most stable structure occurs at size 13, which corresponds to complete Mackay icosahedra [59]. The other relatively more stable structures with respect to their neighbouring sizes are \( N = 38, 50, 54, 61, 68 \) and 75 corresponding to truncated octahedron, twinned truncated octahedron, uncentred icosahedra [60] and some other three fcc structures, respectively.

3.2. Gold clusters

Gold nanoparticles are a fundamental part of the recently synthesized novel nanostructured materials and devices [61–63]. Structural characterization using a variety of experimental
Figure 2. Structures of the global minima for Al7–Al80 clusters.
techniques can be performed on Au clusters [64–68]. Experiments suggest that gold nanoclusters with diameters of 1–2 nm, corresponding to aggregates with \( N = 20–200 \) atoms, are amorphous [64, 65]. The theoretical studies on gold nanoclusters change from empirical MD or MC simulations using EAM [69], Gupta [70, 71], Sutton–Chen [15] and Murrell–Mottram [72] potentials to some first-principle calculations using DFT [73, 74], generalized gradient approximation [75], spin-polarized Becke–Lee–Yang–Parr functional [76] and Hartree–Fock and post-Hartree–Fock levels [77].

We have reported the total energies \( (E) \), the PG and the SA (whenever possible) of the global minima for the gold clusters of \( N = 2–80 \) atoms described by the Voter–Chen potential in table 2. The energies and the second finite differences in energies are plotted in figures 3(a) and (b), respectively. The triangulated polyhedral structures of the Au7–Au80 global minima are illustrated in figure 4. In our calculations we have found that Au9–Au14 clusters are icosahedral. The 13-atom icosahedron has been reported as the lowest energy structure of a Au13 cluster by some of the previous empirical studies [15, 72] as well, although they have presented different structures for some of the gold clusters in this size range. However, the icosahedron is not the global minimum in the first principle calculations of Wang et al. [74]. In addition, in many of the \textit{ab initio} studies, planar forms are found to be the lowest energy structures of the smaller clusters [73–75], since the empirical many-body methods lack directionality, and as a result, these potentials favour more compact and spherically symmetric structures. However, this discrepancy between the first principle and empirical methods vanishes when the cluster size increases. In our results the global minima of Au15, Au16, Au18 and Au19 are the same as those of the corresponding Al clusters. Akin to the Al clusters, in the size range of \( N = 20–36 \), all gold clusters have f3I structures. The 37-atom cluster has a mixture of decahedral and icosahedral morphologies. The 38-atom cluster is a truncated octahedron. We have found only two more fcc structures (at \( N = 61 \) and 79) as the global minima of Au clusters above this size. In agreement with many of the previous theoretical calculations, the Au55 is not an icosahedron in our calculations too, although 52-, 53- and 54-atom Au clusters are ucI. For the size range of \( N = 64–79 \), the dominant structural motif is the decahedral morphology. Although the 64-, 71- and 75-atom clusters have perfect decahedral structures, the 66-, 72-, 73-, 74-, 76- and 77-atom clusters have some icosahedral deficiencies on their decahedral backbones. Our results for the Au clusters are in agreement with the previous theoretical [70] and experimental suggestions that gold nanoclusters with \( N = 20–200 \) atoms are amorphous [64, 65] since most of the structures reported in this work have low symmetry (i.e. \( C_s \)). Figure 3(b) suggests that the most stable structures occur at sizes of 13, 30, 40, 54, 66, 73, 75, 77 and 79. The 38-atom truncated octahedron does not seem as a magic number of the Au clusters, instead a 40-atom amorphous structure is more stable. For the higher sizes, decahedral structures and mixtures of decahedral and icosahedral staking sequences become more stable than the others, except the 54-atom uncentred icosahedron and 79-atom truncated octahedron.

### 3.3. Platinum clusters

We have previously reported the lowest energy structures, number of stable isomers, growth pathways, probabilities of sampling the basins of attraction of the stable isomers and the energy spectrum-widths which are defined by the energy difference between the most and the least stable isomers of Pt2–Pt31 clusters [57] and the global minima of Pt32–Pt56 clusters [60]. Since all the relevant literature on platinum clusters can be found in those studies, we do not repeat them again here. We have reported the \( E \), the PG and the SA of the global minima of Pt clusters described by the Voter–Chen potential for \( N \leq 80 \) atoms in table 3. The energies and
Global minima of Al$_N$, Au$_N$ and Pt$_N$ clusters

Table 2. Global minima for Au clusters. For each minimum energy ($E$), PG and SA are given if possible. The structural categories are: centred (cI), ucl and fdI; packed fcc; decahedral with $n$ atoms along the decahedral axis (dec$(n)$); involving a mixture of stacking sequences (mix).

| $N$ | $E$ (eV) | PG | SA | $N$ | $E$ (eV) | PG | SA |
|-----|---------|----|----|-----|---------|----|----|
| 2   | −2.2886 | $D_{5h}$ | cl | 41  | −138.2008 | c$_1$ | fdI |
| 3   | −5.2797 | $D_{3h}$ | cl | 42  | −141.9077 | c$_4$ | fdI |
| 4   | −8.8497 | $T_g$  | cl | 43  | −145.4197 | c$_8$ | |
| 5   | −12.1736 | $D_{3a}$ | 44  | −149.0400 | c$_{10}$ | |
| 6   | −15.8281 | $O_h$  | fcc | 45  | −152.6610 | c$_{18}$ | |
| 7   | −19.1505 | $D_{3a}$ | 46  | −156.2059 | c$_{20}$ | |
| 8   | −22.4326 | $D_{2d}$ | 47  | −159.8067 | c$_{24}$ | |
| 9   | −25.7507 | $C_{2v}$ | cl | 48  | −163.4242 | c$_{28}$ | |
| 10  | −29.1712 | $C_{3v}$ | cl | 49  | −167.0450 | c$_{30}$ | |
| 11  | −32.4968 | $C_{2v}$ | cl | 50  | −170.5777 | c$_{32}$ | |
| 12  | −36.0088 | $C_{3v}$ | cl | 51  | −174.1304 | c$_{34}$ | |
| 13  | −40.1043 | $I_h$  | cl | 52  | −177.9191 | $C_{2h}$ | ucl |
| 14  | −42.9943 | $C_{3u}$ | cl | 53  | −181.7385 | $C_{5v}$ | ucl |
| 15  | −46.9690 | $D_{5h}$ | 54  | −185.5635 | $I_h$  | ucl |
| 16  | −50.1275 | $C_{3v}$ | 55  | −188.6971 | $C_{6v}$ | |
| 17  | −53.5914 | $C_{3v}$ | 56  | −192.2661 | $C_{8v}$ | |
| 18  | −56.9242 | $C_{4v}$ | mix | 57  | −195.8573 | $C_{12v}$ | |
| 19  | −60.3352 | $D_{3h}$ | cl | 58  | −199.4305 | $C_{15v}$ | |
| 20  | −63.7463 | $C_{2h}$ | fsl | 59  | −202.9304 | $C_{18v}$ | |
| 21  | −67.2933 | $C_{2v}$ | fsl | 60  | −206.6851 | $C_{20v}$ | |
| 22  | −70.9625 | $C_{1v}$ | fsl | 61  | −210.3464 | $C_{24v}$ | fcc |
| 23  | −74.5236 | $C_{1v}$ | fsl | 62  | −213.9025 | $C_{28v}$ | |
| 24  | −77.9539 | $C_{1v}$ | fsl | 63  | −217.5417 | $C_{32v}$ | |
| 25  | −81.3036 | $C_{1v}$ | fsl | 64  | −221.2176 | $C_{42v}$ | dec$(5)$ |
| 26  | −84.8046 | $C_{1v}$ | fsl | 65  | −224.9052 | $C_{48v}$ | |
| 27  | −88.4414 | $C_{1v}$ | fsl | 66  | −228.6560 | $C_{56v}$ | mix |
| 28  | −92.0749 | $C_{1v}$ | fsl | 67  | −232.1324 | $C_{64v}$ | |
| 29  | −95.5729 | $C_{1v}$ | fsl | 68  | −235.8811 | $C_{72v}$ | |
| 30  | −99.2318 | $C_{1v}$ | fsl | 69  | −239.5284 | $C_{80v}$ | |
| 31  | −102.5796 | $C_{1v}$ | fsl | 70  | −243.1537 | $C_{90v}$ | |
| 32  | −106.1560 | $D_{2d}$ | fsl | 71  | −246.8875 | $C_{100v}$ | dec$(5)$ |
| 33  | −109.6664 | $C_{1v}$ | fsl | 72  | −250.5921 | $C_{120v}$ | mix |
| 34  | −113.2711 | $C_{1v}$ | fsl | 73  | −254.3504 | $C_{160v}$ | mix |
| 35  | −116.8575 | $C_{1v}$ | fsl | 74  | −257.8233 | $C_{192v}$ | mix |
| 36  | −120.4893 | $C_{2v}$ | fsl | 75  | −261.6719 | $D_{5h}$  | dec$(5)$ |
| 37  | −124.0150 | $C_{2v}$ | mix | 76  | −265.2637 | $C_{240v}$ | mix |
| 38  | −127.6334 | $O_h$  | fcc | 77  | −269.0221 | $C_{288v}$ | mix |
| 39  | −131.1339 | $C_{1v}$ | fsl | 78  | −272.4326 | $O_h$  | fcc |
| 40  | −134.8451 | $C_{1v}$ | fsl | 79  | −276.2856 | $O_h$  | fcc |

the second finite differences in energies are plotted in figures 5(a) and (b), respectively. The triangulated polyhedral structures of the Pt$_7$–Pt$_{80}$ global minima are illustrated in figure 6. The lowest energy structures of the Pt clusters are more similar to the Au clusters than those of the Al clusters. All the global minima of Au and Pt clusters are identical for $N \leq 17$. The 18-atom Pt cluster does not have the decahedral morphology of the Au$_{18}$ cluster. In the size range of $N = 19$–38, most of the Pt clusters have ucl structures which are similar to both Al and Au clusters. In this size range, 12 Pt clusters have identical structures with the corresponding Au clusters (i.e. at the sizes of 19–21, 26, 28–30, 32, 33, 36–38). The main differences between
Figure 3. (a) $E - E_0$ is the relative energies of quenched Au clusters, where $E_0 = 8.71376 - 6.98547N^{2/3} + 4.0186N^{2/3} - 4.16303N$; (b) the second finite difference, $D_2$, in binding energy versus size $N$.

The Au and Pt clusters occur at the sizes of 41, 50, 51, 55, 70, 74, 76, 78 and 80: the 41-atom Pt cluster has a mixture of decahedral and icosahedral morphologies, the 50-atom Pt cluster is a twinned truncated octahedron, the 51-atom cluster is an uncentred icosahedron missing three surface atoms, the 55-atom cluster is a complete Mackay icosahedron, the 70-, 74- and 76-atom clusters are some decahedrons and finally the 78- and 80-atom Pt clusters have a mixture of decahedral and icosahedral staking sequences. For the higher sizes, while Pt clusters prefer fully decahedral structures, the Au clusters favour structures involving a mixture of decahedral and icosahedral staking sequences (see the sizes of 70, 74 and 76). When the normalized energy (figure 5(a)) and the second finite difference in energy plots (figure 5(b)) of the Pt clusters are considered, it can be seen that the most stable sizes are 13, 38, 50, 54, 61, 68 and 75. Interestingly, these magic numbers are more similar to those of the Al than those of the Au clusters.

The issue of the effect of the cluster’s symmetry on the reaction kinetics has been studied by Jellinek and Güvenç [7] before. Most recently Böyükata et al [78] have studied the
Global minima of Al$_N$, Au$_N$ and Pt$_N$ clusters.

Figure 4. Structures of the global minima for Au$_7$–Au$_{80}$ clusters.
structure and reactivity relations of Ni clusters. The reactivity of Al, Au and Pt clusters with diatomic molecules can be discussed in a future work where the structures reported here will be very useful.

4. Summary

In this study we have reported the global minima of Al, Au and Pt clusters up to 80 atoms described by the Voter–Chen version of the EAM potential using the basin-hopping
MC geometry minimization technique. Our aim is to study the structural and energetic properties of the series of three metal clusters and to identify their most possible lowest energy structures by searching nearly the whole set of known low-lying minima, which is extremely difficult to achieve, using more accurate descriptions of the interatomic interactions.

The results obtained in this study show that the global minima of the Al, Au and Pt clusters have structures based on either fcc, decahedral, icosahedral or a mixture of decahedral and icosahedral packing. The 54-atom icosahedron without a central atom is found to be more stable than the 55-atom complete icosahedron for all of the elements considered in this work. Most of the Al global minima are identified as some fcc structures as the previous experimental studies suggest. Many of the Au global minima are found in low symmetric forms, which is also in agreement with the theoretical and experimental studies of the Au clusters. Although many of the Pt global minima are identical with the global minima of the corresponding Au clusters, the most stable sizes of the Pt clusters occur at the same sizes as the Al clusters.
Figure 6. Structures of the global minima for Pt7–Pt80 clusters.
In this paper, we would like to invite the attention of the cluster science community to the Voter–Chen EAM interatomic potentials of transition metals and Al, which are not only successful in the characterization of the different structures of the clusters qualitatively (i.e. fcc packed for Al, low symmetric for Au and Pt) but also provide more reliable quantitative results of the binding energies and bond lengths for the small clusters.

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