Structural Transition from Icosahedra to Decahedra of Large Lennard-Jones Clusters

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The lowest icosahedral and decahedral energies of LJ1001−1610 clusters are obtained using a greedy search method (GSM) based on lattice construction. By comparing the lowest energies of icosahedral and decahedral clusters with the same atoms, the structural transition of LJ clusters is studied. Results show that the critical size from icosahedra to decahedra is located at $N = 1034$. When the cluster size is larger than 1034, the optimal structures are decahedra except the LJ1367−1422 clusters near the magic number, 1402, of icosahedra. However, the energies of icosahedra near the next magic number, 2044, are higher than that of decahedra, which implies that decahedra will be the optimal structure when the cluster size is larger than 1422, even for those clusters near the magic numbers of icosahedra.

Introduction

Atomic clusters (i.e., finite aggregates of up to tens of thousand of atoms) exhibit unique physical and chemical properties. The dependence and evolution of these properties with size are investigated increasingly to elucidate the transition from atoms to bulk material. Lennard-Jones (LJ) clusters represent one such test system with the potential

$$E = 4\epsilon\sum_{i<j}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

where r_{ij}, ϵ, and $2^{1/6}\sigma$ are the distance between atoms i and j, the pair well depth, and the equilibrium pair separation, and $\epsilon = \sigma = 1$ with reduced units is used. The reported results of LJ clusters showed that the structures of smaller LJ clusters are icosahedral, decahedral packing with noncrystalline 5-fold symmetry,[1,2] which are completely different from the bulk crystalline face-centered cubic (fcc) structures. Therefore, it is natural to ask at what cluster size the icosahedra or decahedra will transform to fcc, which is a significant issue in researching the growth process of clusters.

Experimental research on structural transitions of LJ clusters is ascribed to their electron diffraction data. Using such methods, Farges et al.[2] studied the transition from icosahedra to a bulklike structure. The results showed that the transition occurs for systems larger than approximately 750 atoms. Lee and Stein[3] reported a crossover between a size of 1500 and 3500 atoms for LJ clusters at somewhat colder temperatures than that of Farges et al. The size difference is due to the fact that the cluster size distribution in a beam is relatively broad and can only be known approximately. The exact relationship between these structural isomers and the lowest energy structure is somewhat unclear. Therefore, the study on the size of the structural transition is likely to remain a theoretical question.

One theoretical method is to build structural models of magic numbers and compare the energy of icosahedra with fcc clusters with the same size. Because the cuboctahedra have the same number of atoms per closed shell as the icosahedral structure, this structure is often used as a comparison with icosahedra to study the structural transition from icosahedra to the fcc bulk structure. The compared results of Xie et al.[4] showed that the icosahedral structure remained more favorable up to some 10^4 atoms; Lee and Stein[3] also reported their results by energy minimization calculations on LJ clusters with the crossover size about 3000 atoms. However, the favorable shape of fcc bulk crystals is not cuboctahedra but truncated octahedra (Wulff-polyhedron or tetrakaidecahedron). Therefore, the transition from icosahedra to truncated octahedra was studied by extrapolating a simple function of the energy difference between icosahedra and truncated octahedra (fcc) with the size of the cluster; the crossing point between the straight line of the function and the zero abscissa is the critical size of the structural transition.[5] Using this method, Van de Waal estimated that the critical size occurs at a size between 3000 and 4000 atoms for LJ clusters.

Another theoretical method is the molecular dynamics method, which also has been employed to study the transition from the icosahedra to fcc. Results showed that a LJ cluster at zero temperature must contain at least 5000 atoms before the fcc structure becomes more stable than that of the Mackay icosahedra.[6]

The structural transition of LJ clusters from icosahedra to the fcc structure had been studied extensively and was summarized by Hartke.[7] However, the decahedral motif was omitted because of instability of Ino's decahedra. The particle shape as a decahedron has often been observed by microscopy in a wide size range in metal clusters.[8,9] Motivated by the experimental results, a modified Wulff construction was introduced by Marks[9,10] to model the Mark's decahedron. The reentrant faces at the twin boundaries of the decahedron decrease its surface energy and make it a competitive structural motif in the medium size range. Therefore, it is natural to ask whether the stable motif has been transformed to Marks' decahedra before the clusters are transformed into the fcc structural motif.

One of the recent works on a complete study of the LJ system was done by Raoult et al.[8] The crossover point from icosahedral to Mark's decahedral motif was estimated by comparing the lowest energy sequence (i.e., a sequence composed of the lowest

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energies of the clusters only at the magic numbers). The results showed that when the size is larger than 1600, the stable LJ sequence is a decahedral motif. However, the results of our previous studies showed that the number of decahedral structures in the size range of 562−1000 atoms increases with an increase of cluster size. Moreover, the lowest energy sequence of icosahedra severely overestimates the icosahedral stability of LJ clusters as compared with that of decahedra.[11] Therefore, the structural transition studied only by comparing the lowest energy sequence may be inadequate.

For geometric optimization of clusters, two kinds of methods are generally used (i.e., the unbiased global optimization methods and the biased algorithms incorporated with some known structural knowledge). The former makes no assumptions regarding cluster geometry, such as genetic algorithms,[12−14] simulated annealing,[15] Basin-Hopping,[16] conformational space annealing (CSA),[17] hierarchical global optimization,[18] fast annealing evolutionary algorithm,[19] random tunneling algorithm (RTA),[20] dynamic lattice search (DLS),[21] etc., and the later one generally combines the optimization strategies with lattice construction[22−27] because modeling can make the optimization much easier. Although the global optimization methods had been successfully applied to cluster optimization, when the cluster size is large, the optimization only by searching strategies cannot be sufficient. In this paper, to investigate the definitive crossover point and find out the growth rule of LJ clusters, the lowest energies of icosahedra and decahedra are obtained with a greedy search method (GSM)[11] based on lattice construction. By comparing the energies of the two configurations with the same size, it is found that the two structural motifs compete fiercely near LJ1027 and that the decahedral motifs are predominant when the cluster size is larger than $N = 1034$ except some icosahedra near its magic number, 1402. However, the optimal structures of LJ clusters near the next icosahedral magic number, 2044, are Mark's decahedra.

Methods

The GSM based on lattice construction is developed for optimization of large LJ clusters, its details has been introduced in our previous paper.[11] The structure with the lowest energy can be obtained by searching the appropriate sites for atoms to be occupied among the icosahedral or decahedral lattice. The main procedures can be summarized as follows. (1) At first, an icosahedral or decahedral lattice was constructed, and an initial configuration based on the constructed lattice was generated. The N_c atoms were placed on the lattice sites of an icosahedral or decahedral core, and then the $N-N_c$ atoms are distributed randomly on the remnant N_s-N_c sites. (2) Then, the energy of each lattice site was calculated by using the Lennard-Jones potential based on the coordinates of the icosahedron or decahedron, respectively. (3) According to the energies, the atom with the highest energy was moved iteratively to the unoccupied site with the lowest energy until the total energy did not change. Because this method was not deterministic but stochastic, it may converge at various configurations. Therefore, to find the structure with lowest energy, the GSM procedure was repeated for 100 000 or more independent runs from different random starting configurations. (4) Because of the asymmetry of the outer atoms, the force exerted onto the core was not symmetric, and the positions of the atoms may deviate slightly from the lattice sites. A local minimization technique, a limited memory BFGS (L-BFGS),[28] is applied to obtain the final structure of the LJ cluster.

In GSM, the search space was reduced by fixing the inner lattice sites because the growth of icosahedral and decahedral clusters was generally from inner to outer shells. The method was generally named as a seeding technique in conventional algorithms, which was very helpful for the structural optimization of clusters and had been employed in many works of clusters optimization.[13,16,20,29] However, the candidate lattice sites on the outermost shell increase remarkably with the increase of the shell of the icosahedron and decahedron. For example, the outermost shell of icosahedra was composed by $10l^2 + 2$ lattice sites (l is the number of icosahedral shell). Therefore, the optimization is also time-consuming.

In this study, to further narrow the search space, the candidate lattice sites were reasonably limited. For icosahedra, the search space can be easily further narrowed according to the growth characteristic obtained from the small clusters because icosahedra are symmetric structures. For example, to optimize LJ1000 clusters, the lattice sites of all the inner shells except for the vertexes of the outermost inner shell were fixed as the seeding sites. Furthermore, due to its symmetric property, it was enough to choose only half of the lattice sites on the outermost shell for this cluster.

Furthermore, the lattice of decahedra was difficult to choose for the optimization of large LJ clusters because decahedral configurations include three main shapes: approximately spherical decahedra, oblate, and prolate decahedra, which are known from the optimal decahedral structures of the LJ562−1000 clusters in our previous work.[11] It was too time-consuming if a large enough decahedral lattice simultaneously containing all the three shapes was used because too many candidate sites needed to be searched in the optimization. From the configuration of Inos' decahedron in Figure 1, it can be seen that the ratio of the horizontal and radial radii is approximately equal to 1: $\sqrt{2}$. However, the optimal configurations of clusters tend to grow spherically. Therefore, in this paper, to further reduce the search space, three decahedral lattices containing relatively few lattice sites with similar ratios (approximately spherical, oblate, and prolate decahedra) are used, respectively, as the lattice (i.e., at first, to find the lowest energy of the three shapes separately, and then, by comparing the energies of the three Mark's decahedra, the structure with the lowest energy is taken as the final result).

Generally, a truncated tetrahedron and truncated octahedron should also be included in the structural motifs of Lennard-Jones clusters. However, because the truncated tetrahedron is not energetically competitive for large clusters,[30] it should not exist in the studied size range. As for the truncated octahedron, it was reported that only LJ clusters near the magic numbers have the possibility of being a favorable structure.[8] Therefore, in this study, the truncated tetrahedron and truncated octahedron motifs are not included in our optimization; however, the energies of the truncated octahedra at magic numbers reported in the literature[8] were used in the discussion.

Results and Discussion

Optimization Results Based on Icosahedral Lattice.

According to the reported works,[8] icosahedral configurations are favored when the size is less than 1600 for LJ clusters. Therefore, the icosahedral structures are optimized using the proposed method. To validate the optimized results, the variation of the first finite difference of energy $\Delta E = E(N) - E(N-1)$ is plotted versus the clusters size N in Figure 2. From the figure, it can be found that the ΔE values are in a normal range, which suggests that the putative minima of the icosahedra should be reasonable, although further verification or proofing is still needed. Furthermore, it can be seen from the figure that LJ1367,

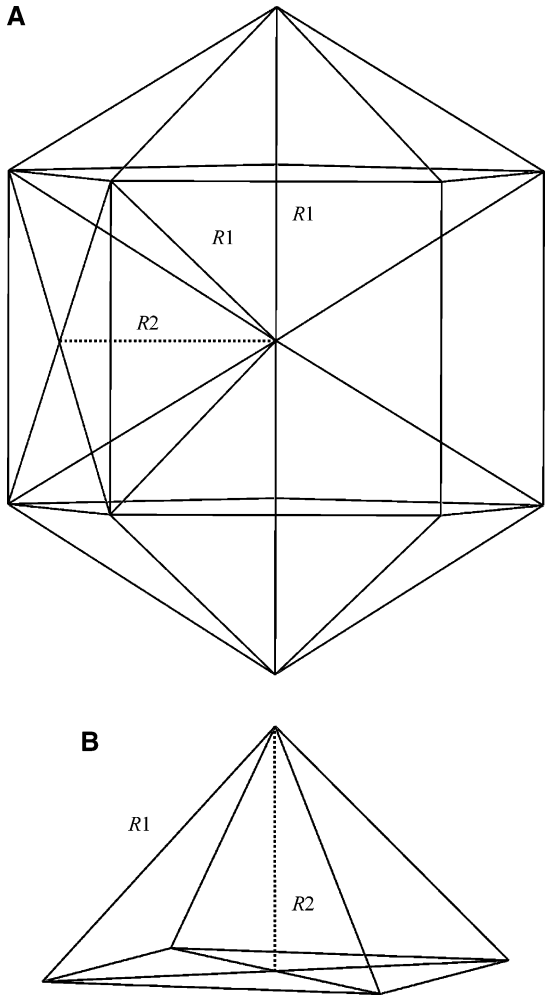

Figure 1. Configuration of Inos' decahedron. (a) The radial and horizontal radii, $r1$ and $r2$, of Ino's decahedron. (b) The quadrangular pyramid taken from Ino's decahedron.

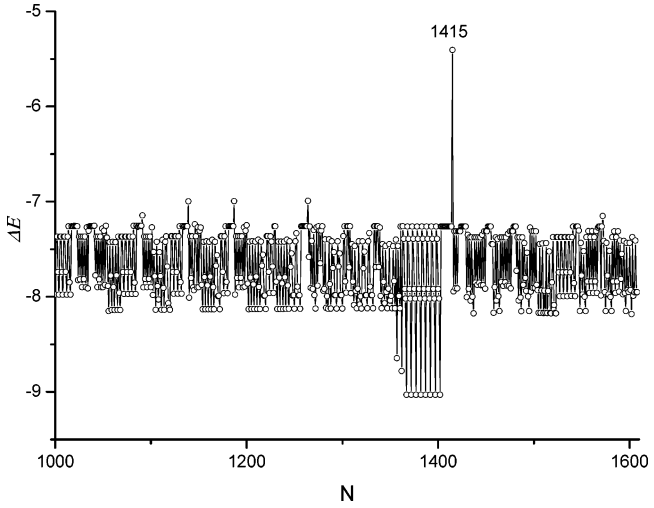

Figure 2. Plot of the variation of the first finite difference of icosahedral energy ΔE vs the cluster size N.

LJ1372, LJ1377, LJ1382, LJ1387, LJ1392, LJ1397, and LJ1402 are very stable. Except for LJ1402, these structures are found to be truncated icosahedra without the vertex atoms and the five atoms around some vertex of the outermost shell, and LJ1402 is found to be a truncated icosahedron without the vertex atoms of the outermost shell. It is worth noting that the increase of the structures without the five atoms around the vertex implies

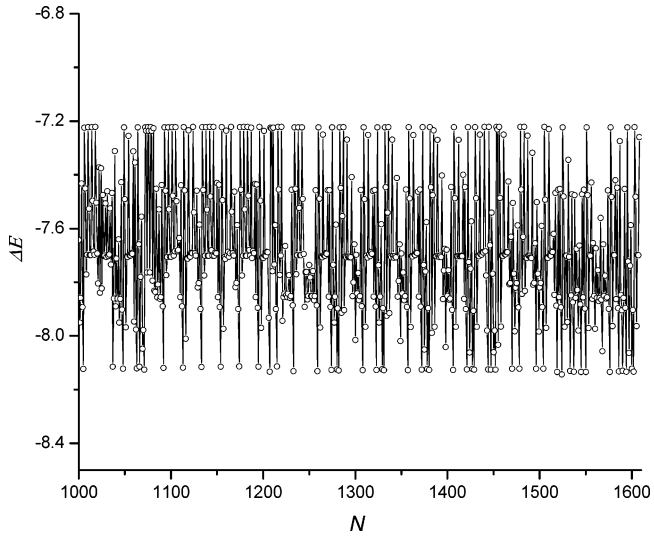

Figure 3. Plot of the variation of the first finite difference of decahedral energy ΔE vs the cluster size N.

that icosahedra tend to grow spherical structures. However, LJ1415 is very unstable because a new shell is added and the atoms on the outermost shell have less neighbor atoms.

On the other hand, because of the effect of the icosahedral strain,[25,31−33] in this work, all the optimal icosahedral configurations are found to be icosahedra with the central vacancy, as even the closed icosahedron, LJ1415, prefers to be a centrally vacant configuration. This can be quantitatively explained by using the equation proposed by Wales.[25]

$$E_{\text{strain}} = \sum_{i<j, r_{ij}<r_0} v(r_{ij}) + 1$$

For example, the mean E_{strain} per atom of LJ1415 with the central vacancy is 0.1982ϵ; however, the mean E_{strain} per atom of LJ1415 without the central vacancy is 0.2544ϵ. Clearly, the central vacancy can relieve the effect of the strain.

Optimization Results Based on Decahedral Lattice.

From the putative global minima of LJ562−1000 clusters,[11] it can be found that the number of decahedral structures increase remarkably as compared with the smaller clusters. To investigate the relative stability of icosahedra and decahedra for larger clusters, the optimal decahedra of the LJ1001−1610 clusters are obtained by using the proposed method. The variation of the first finite difference of energy $\Delta E = E(N) - E(N - 1)$ versus the cluster size N is plotted in Figure 3. From the figure, it can be seen that the ΔE values are located between -7.2ϵ and -8.2ϵ without any extraordinary values. On the other hand, it can also be seen that the average energy differences increase slightly with the increase of cluster size.

The decahedral structures, in this size range, have presented some new characteristics. In previous works,[8,34,35] the notching depth between the (100) faces is defined and represented as s. Decahedral structures with $s = 2$ have been found in the decahedral LJ925 and LJ915 clusters.[11] However, it is found that the number of decahedral structures with $s = 2$ increases with the growth of the clusters, which can be seen from the plane projection of LJ1285 shown in Figure 4a. On the other hand, the top (110) faces are created by removing the eight atoms situated between the capping (111) faces and the (111) re-entrant faces from the Marks decahedra with additional 20 (110) faces, which can be seen from the structure of the outermost shell of the LJ1444 cluster shown in Figure 4b. Some

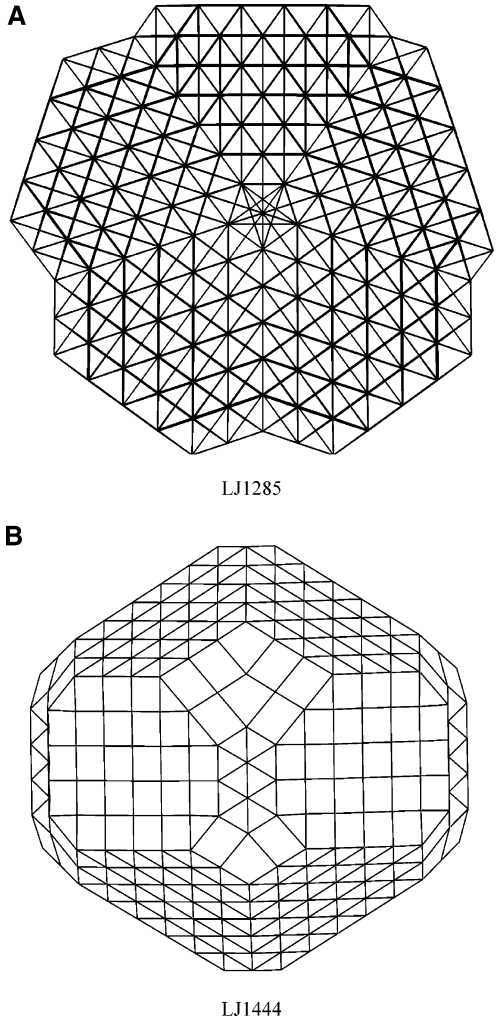

Figure 4. Structural characteristics of the large decahedral structures. (a) The plane projection of LJ1285. (b) The outermost shell of LJ1444.

of these characteristics are consistent with the growth rule of Mark's decahedra.[35]

Structural Transition of LJ Clusters.

To find the structural transition from icosahedra to decahedra, the energies of the LJ560−1610 clusters are plotted in Figure 5, as $(E - E_{oct})/N^{2/3}$ versus N, where E is the energy of Marks' decahedron and icosahedron, and E_{oct} is the four-term least-squares fit to the binding energies of the face centered cubic cuboctahedra.[4] From Figure 5, it is clear that the icosahedral energies, the curve with circle symbols, generally ascend periodically with the increase of the cluster size. On the contrary, decahedral energies, the curve with square symbols, generally descend with the increase of the cluster size. The crossing point of the two energy sequences is the crossover size from the icosahedral to decahedral motifs. To show the definitive crossover size clearly, the energy differences of icosahedra and decahedra versus the cluster size are plotted in Figure 6. From the figure, it is clear that the two structural motifs compete fiercely near LJ1027, that the crossover point is located at $N =$ 1034, when the cluster size is larger than 1034, and that the main structural motif is transformed from icosahedra to decahedra except the LJ1367−1422 clusters, which are located near the magic numbers of icosahedra.

To find whether the energies of icosahedra are lower than that of Mark's decahedra in a large cluster size, the icosahedral and decahedral energies around the next magic number of icosahedra, 2044, are obtained by using the proposed method.

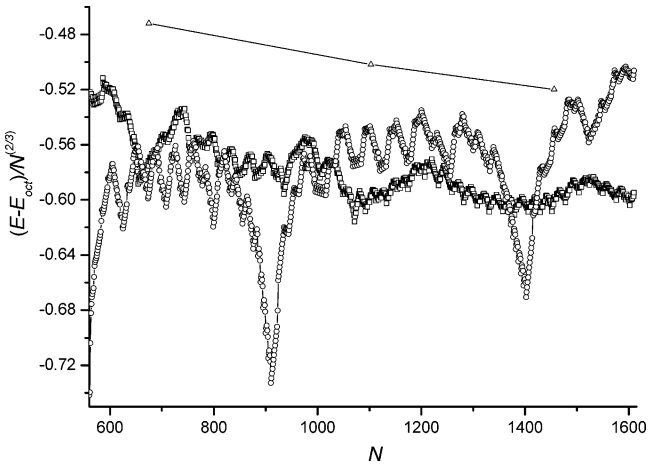

Figure 5. Energy comparison of complete sequence of icosahedra and decahedra. The energy of icosahedron, Marks' decahedron, and truncated octahedron are represented by ○, □, and △, respectively, and E_{oct} is the fitting energy of cuboctahedra.

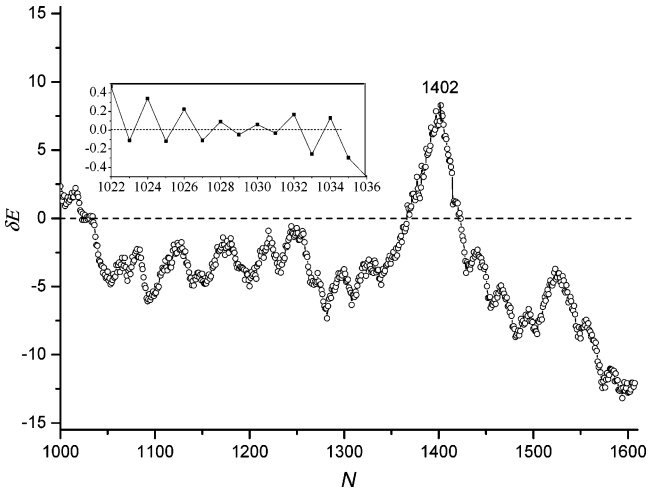

Figure 6. Plot of the energy differences, δE, of icosahedra and decahedra vs the cluster size N.

The results show that the decahedral energies are lower than that of icosahedra. This suggests that the optimal structures of the LJ clusters are no longer an icosahedral motif when the cluster size $N > 1422$.

It is known that the stable structures of bulk material are fcc (truncated octahedra). Therefore, it is natural to think whether the optimal motifs have been transformed to truncated octahedra in the studied size range. The lowest energy sequence of fcc (line with triangle shown as in Figure 5) is compared with the complete energy sequences of icosahedra and decahedra. It can be found that the structural transition from icosahedron to fcc may occur near the truncated octahedral magic number 1456. However, the icosahedral motif should be transformed to the decahedral motif because the complete energy sequence of the decahedron always lies below the lowest energy sequence of the truncated octahedra (i.e., the decahedral structures are more stable than the truncated octahedral structures).

Conclusion

The lowest energies of the LJ1001−1610 clusters with decahedral and icosahedral motifs are obtained, respectively, by using a greedy search method based on lattice construction. By comparing the energies of a LJ cluster with a decahedral and icosahedral motif with the same number of atoms, it is found

that the two structural motifs compete fiercely around LJ1027 and that the decahedral motif is predominant when the cluster size is larger than 1034 except for some icosahedra near the magic number 1402. However, the stable structures of the LJ cluster near the next magic number of the icosahedra are in a decahedral motif, which suggests that the optimal configurations are no longer icosahedral motif when the cluster size is larger than 1422.

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Supporting Information Available: Listing of energies of the putative global minima of LJ1001−1610 clusters. This material is available free of charge via the Internet at http://pubs.acs.org.

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