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To cite this article: Y H Zhu *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **479** 012111

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Theoretical study on the aggregation of aluminium clusters on a silicone oil surface

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Abstract. By using Amsterdam Density Functional (ADF) program based on first-principles, we have in detail investigated the formation mechanism of the aluminium (Al) nanoparticles (NPs) on a silicone oil surface. Our investigation shows that two moving Al clusters on liquid substrate meet to form a random initial structure. Collisions and interactions may make it become a more compact, more stable structure. As the deposition density increases, a disc-shaped morphology would be formed because of isotropy on the silicone oil surfaces. The structures built on the Face-Centered Cubic (FCC) units are not stable. Both atomic displacement and adsorption can almost destroy them. It is difficult to form Al crystals on the silicone oil surfaces.

1. Introduction

The nanoparticles (NPs) of various metal or nonmetal elements on liquid substrate have attracted considerable attentions due to their novel physical and chemical properties. Their optical phenomena [1], quantum confinement [2] and surface plasmon resonances [3] mainly originate from the specific geometrical structures (large-surface area-to-volume ratio, for example), microstructures and compositions of the nanoparticles. Because of these properties, they have many potential applications [4-6].

There are a variety of ways to synthesize two-dimensional or three-dimensional nanoparticle aggregates. Generally, the synthesis can be achieved by physical and chemical means. Although physical methods need complicated equipment, they can be used to fabricate highly pure products in a clean way. On the other hand, chemical methods may produce some harmful by-products, but almost universal. However, Giuffrida *et al.* developed several cheap and fast new approaches of combining the advantages of both physical and chemical methods [7-9].

Although the methods above are used to produce nanoparticles successfully, Ye *et al.* firstly found the nucleation, growth, and aggregation behaviour of silver clusters on silicone oil surfaces [10]. The pioneering work developed a new and simple method to fabricate nanoparticles, nanoparticle aggregates, and continuous thin films using liquid as substrate.

Since then, other liquid substrates have been also employed. For example, Torimoto *et al.* (in 2006) [11] and Wender *et al.* (in 2011) [12] used ionic liquids and vegetable oils as substrates.

Ye *et al.* described the formation mechanism of the aggregates on the liquid substrates by using two-stage growth model [10]. At the first stage, that is, during deposition, disk-shaped clusters are formed. To the second stage, subsequent aggregation of clusters occurs.



In 2014, Pan *et al.* fabricated aluminium nanoparticle (Al NPs) aggregates on silicone oil surfaces at different substrate temperatures by thermal evaporation method [13,14]. It is found that the Al NPs exhibit a disc-shaped morphology with mean diameter and height in the ranges 20–35 and 1.3–3.7 nm, respectively. Atomic force microscopy (AFM) measurement shows that the disc-shaped Al NPs can diffuse and aggregate but seldom overlap each other. As the nominal film thickness increases, the coverage increases at first, then saturates gradually and finally exhibits random fluctuation behaviour with its thickness. The experimental result suggests that the mass density increases during the growth of the Al NPs.

In fact, it is a difficult task to study the deposition mechanism of aluminium clusters on silicone oil surfaces because their morphologies and structures are affected by many factors, such as environmental temperature, time for aggregation and sputtering concentration, etc. In the initial stage of deposition, the deposition structures are also related to the location and orientation of the clusters. This adds to the complexity of the problem.

Fortunately, the silicone oil surfaces are isotropic, and can be generally considered as quasi-free sustained substrates. This is because the metallic atoms on the liquid substrates can diffuse randomly with large diffusion coefficients compared with that on solid substrates.

In this paper, in view of the experimental results, we have performed calculations on the aggregation of the Al clusters at initial stage by using the Amsterdam Density Functional (ADF) program based on first-principles. Our main purpose is to explore their initial growth mechanism.

2. Computational Methods

Firstly, we obtained the ground state structures of the small Al clusters by using the ADF program [15], version (2010.02). Then, two Al clusters are placed in different distances and directions. The bi-cluster system is optimized by the ADF program. See how its microstructure evolves.

In the ADF program, molecular orbitals (MOs) were expanded using a large, uncontracted set of Slater-type orbitals (STOs): Triple-zeta with two polarization functions (TZ2P) [16]. The TZ2P basis is an all-electron basis of triple-z quality, augmented by two sets of polarization functions. The frozen-core approximation for the inner-core electrons was used. The orbitals up to $2p$ for aluminium were kept frozen. An auxiliary set of s , p , d , f , and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials in each self consistent field (SCF) cycle. Calculations have been made in the framework of the generalized gradient approximation (GGA) by means of the Becke-Perdew functional. The method is based on Becke's [17, 18] gradient correction to the local expression for the exchange energy and the correlation energy. The self-consistent field was converged to a value of 10^{-4} .

3. Results and discussion

3.1. Experimental results [13,14]

The experimental results in our group reveal that the morphologies of the Al NPs aggregates seldom overlap each other at the initial stage with a nominal film thickness h equal to 0.02. As h increases, the number density increases rapidly. The Al NPs, which diffuse randomly on the liquid surface, would form fractal aggregates once they meet. After $h \geq 0.10$ nm, the aggregates connect with each other and finally form a net-shaped or a nearly continuous film. The phenomenon helps us to reveal the growth mechanism of the Al system.

3.2. Aggregation of the small Al_n clusters

The investigation on the small Al clusters shows that they begin to transfer from planar structures to three dimensional structures at $n=6$. The binding energies (BE , in eV), electron affinities (EA , in eV), ionization potentials (IP , in eV) and some relevant experimental data can be found in some published articles [19-27]. The ion clusters Al_7^+ , Al_{13}^- and Al_{19}^- exhibits higher stability. Their stabilities can be explained well by spherical jellium model (SJM) [20].

Aggregation of the small Al_n clusters has been investigated by the ADF program. The process of several identical or different clusters approaching in different directions is simulated. We want to know how they aggregate together, and what kind of stable structures can be formed. Here, the Al_{13} and Al_{19} clusters are taken as examples to illustrate their microscopic mechanism.

The Al_{13} and Al_{19} clusters can be obtained in many channels. For example, $Al_6 + Al_7 \rightarrow Al_{13}$, $Al_6 + Al_6 + Al_1 \rightarrow Al_{13}$, $Al_6 + Al_6 + Al_7 \rightarrow Al_{19}$, $Al_{13} + Al_6 \rightarrow Al_{19}$, and so on. The aggregates from smaller Al clusters are mostly meta-stable structures. There is a potential barrier between them, and most of them are difficult to transfer spontaneously from one structure to another. But, some structures are influenced by exoteric factors, and sometimes can change from meta-stable states to more stable states. This process may occur many times. The first structural transformation is easier because an initial structure formed by random is relatively relaxed. But as structural tightness increases, the structural change is getting harder and harder. This is consistent with the two-stage growth model.

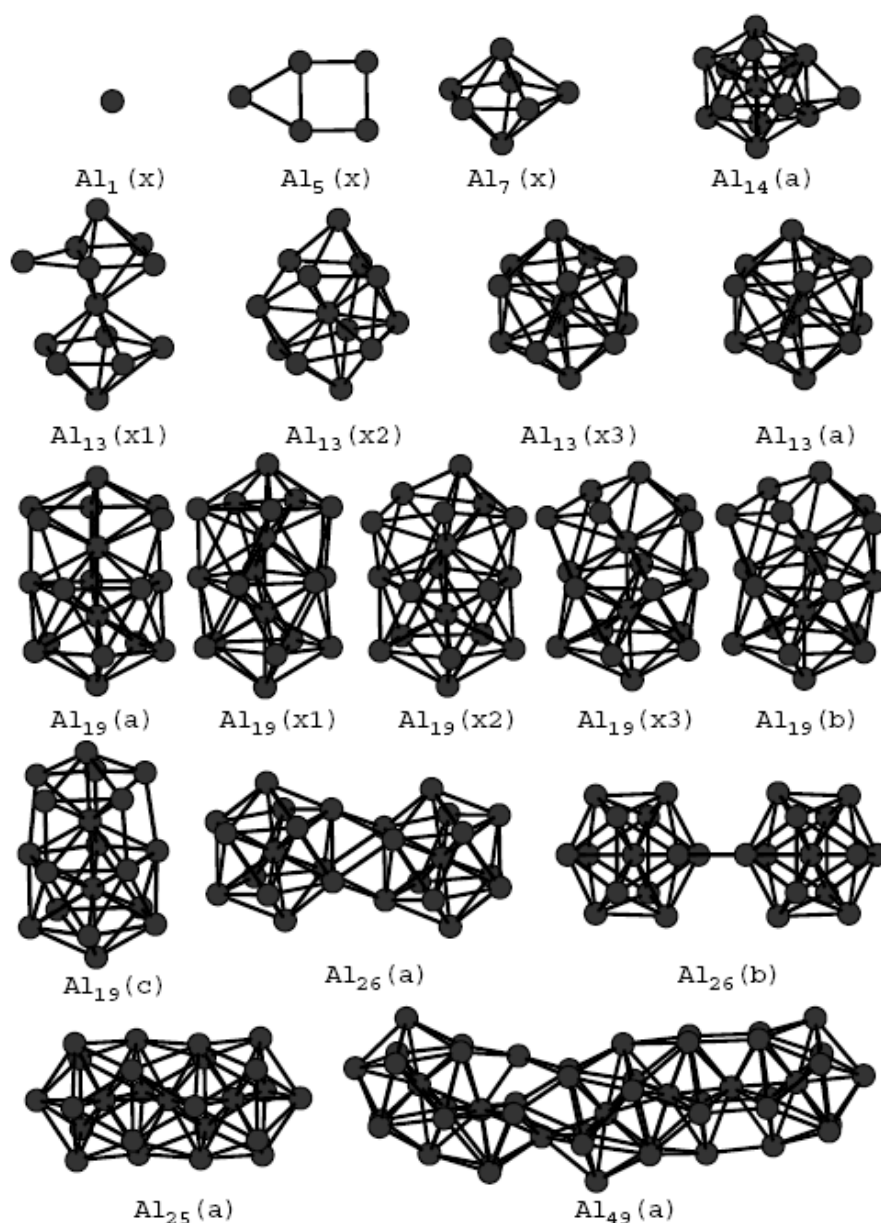


Figure 1. Some representative stacked structures and partial evolution processes.

The ground state structure of the Al_{13} cluster is a distorted icosahedral cage with one central atom (see $\text{Al}_{13}(\text{a})$ in figure 1). We try to construct its initial structure by using two Al_5 structures and 3 atoms. After structural optimization, the ground state structure $\text{Al}_{13}(\text{a})$ can be obtained. Sometimes, it is difficult to get it directly from the ground state structures of two smaller clusters. For example, we cannot get the ground state structure $\text{Al}_{13}(\text{a})$ directly by combining the lowest energy structures Al_6 and Al_7 . But it can be obtained by other channels. Two smaller meta-stable structures are more likely to form its ground state structure. For example, both the pentagonal bipyramid $\text{Al}_7(\text{x})$ of the Al_7 cluster and the pentagon plane structure $\text{Al}_5(\text{x})$ of the Al_5 cluster in figure 1 are meta-stable structures. The initial structure $\text{Al}_{13}(\text{x}1)$ in figure 1 is based on the two meta-stable structures $\text{Al}_7(\text{x})$, $\text{Al}_5(\text{x})$ and one atom $\text{Al}_1(\text{x})$. In the process of its structural optimization, its two intermediate structures $\text{Al}_{13}(\text{x}2)$ and $\text{Al}_{13}(\text{x}3)$ are also presented in figure 1. It can be seen here how it evolves from the initial structure $\text{Al}_{13}(\text{x}1)$ to the final stable structure $\text{Al}_{13}(\text{a})$. But, some initial stacking structures are difficult to evolve to the predicted structure because of the potential barrier.

The $\text{Al}_{19}(\text{a})$ in figure 1 is the ground state structure of Al_{19} cluster. The structure $\text{Al}_{19}(\text{x}1)$ in figure 1 is obtained by stacking $\text{Al}_{13}(\text{a})$, $\text{Al}_5(\text{x})$ and $\text{Al}_1(\text{x})$. After it is optimized, one stable structure $\text{Al}_{19}(\text{b})$ is obtained. Two intermediate structures $\text{Al}_{19}(\text{x}2)$ and $\text{Al}_{19}(\text{x}3)$ are also presented in figure 1. The $\text{Al}_{19}(\text{b})$ lies 0.16 eV higher in energy than the $\text{Al}_{19}(\text{a})$. If the structure $\text{Al}_5(\text{x})$ in $\text{Al}_{19}(\text{x}1)$ is rotated 180 degree around the axis perpendicular to its plane, one new initial structure will be produced. After structural optimization, another stable structure $\text{Al}_{19}(\text{c})$ in figure 1 is obtained. It is 0.32 eV less stable than the $\text{Al}_{19}(\text{a})$. The potential barrier from the $\text{Al}_{19}(\text{c})$ to the $\text{Al}_{19}(\text{a})$ is 0.15 eV. It is relatively easy to convert from the $\text{Al}_{19}(\text{c})$ to the $\text{Al}_{19}(\text{a})$.

For other given clusters, there are such similar phenomena. When any two Al clusters on liquid substrate meet in the course of the movement, they would form the initial structure of a larger cluster. So their formation is random. Meanwhile, they will gradually become more stable and more compact from looser structures because of collisions and interactions. Of course, the opposite process can also be produced in theory. But, it is hard to be observed in experiment because the compacted clusters or branched aggregates are not easy to disintegrate, or the probability of disintegration is very small. Therefore, with the increase of the deposition density, the aggregation probability is increasing.

Again, both of the $\text{Al}_{26}(\text{a})$ and $\text{Al}_{26}(\text{b})$ in Figure 1 are stacked by the ground state structure $\text{Al}_{13}(\text{a})$. They meet in different directions. As a result, their stable structures are different. It is hard for an arbitrary loose structure to change directly into the corresponding ground state structure because there are several meta-stable structures, and potential barriers between them in the process of structural transformation. Some structures may never be transferred into their ground state structures.

In addition, some structures stacked along one dimension will bend as their lengths increase. The $\text{Al}_{25}(\text{a})$ in figure 1 is stacked from two icosahedrons sharing a top atom. The initial structure of the $\text{Al}_{49}(\text{a})$ in figure 1 consists of two $\text{Al}_{25}(\text{a})$ sharing a top atom, or four icosahedrons sharing three top atoms. Its final geometric configuration has undergone a serious distortion.

At a certain temperature, the microstructure of the aggregations is different because the cluster structures change with size and they form different initial morphologies. But, the liquid surface is two-dimensional isotropic. Therefore, it is easier to understand that the Al NPs on liquid substrate exhibit a disc-shaped morphology.

3.3. The possibility of Al crystal formation

It is known that the crystal structure of metallic aluminium is Face-Centered Cubic (FCC). Its lattice constant is 4.05 Å. The unit cell optimized by the ADF program is shown as $\text{Al}_{14}(\text{x})$ in figure 2. Obviously, it has undergone a slight structural distortion compared to the perfect FCC. In addition, it lies 3.60 eV higher in energy than the ground state structure $\text{Al}_{14}(\text{a})$ of Al_{14} cluster. This is a larger energy difference for the cluster with only 14 atoms. Its corresponding energy difference per atom is 0.26 eV. So the unit cell is difficult to be stable. But the stability of the structures built on the FCC units increases gradually as the number of the unit cells increases.

Both $\text{Al}_{23}(\text{a})$ and $\text{Al}_{23}(\text{x})$ include 23 atoms. The former is composed of two icosahedral structures sharing one face. It is the lowest energy structure of Al_{23} cluster obtained by the ADF program. The latter consists of two FCC units. After structural optimization, some distortion occurs. The latter is less stable than the former with energy difference $\Delta E = 3.45$ eV. Its corresponding energy difference per atom decreases down to 0.15 eV. Its relative stability increases.

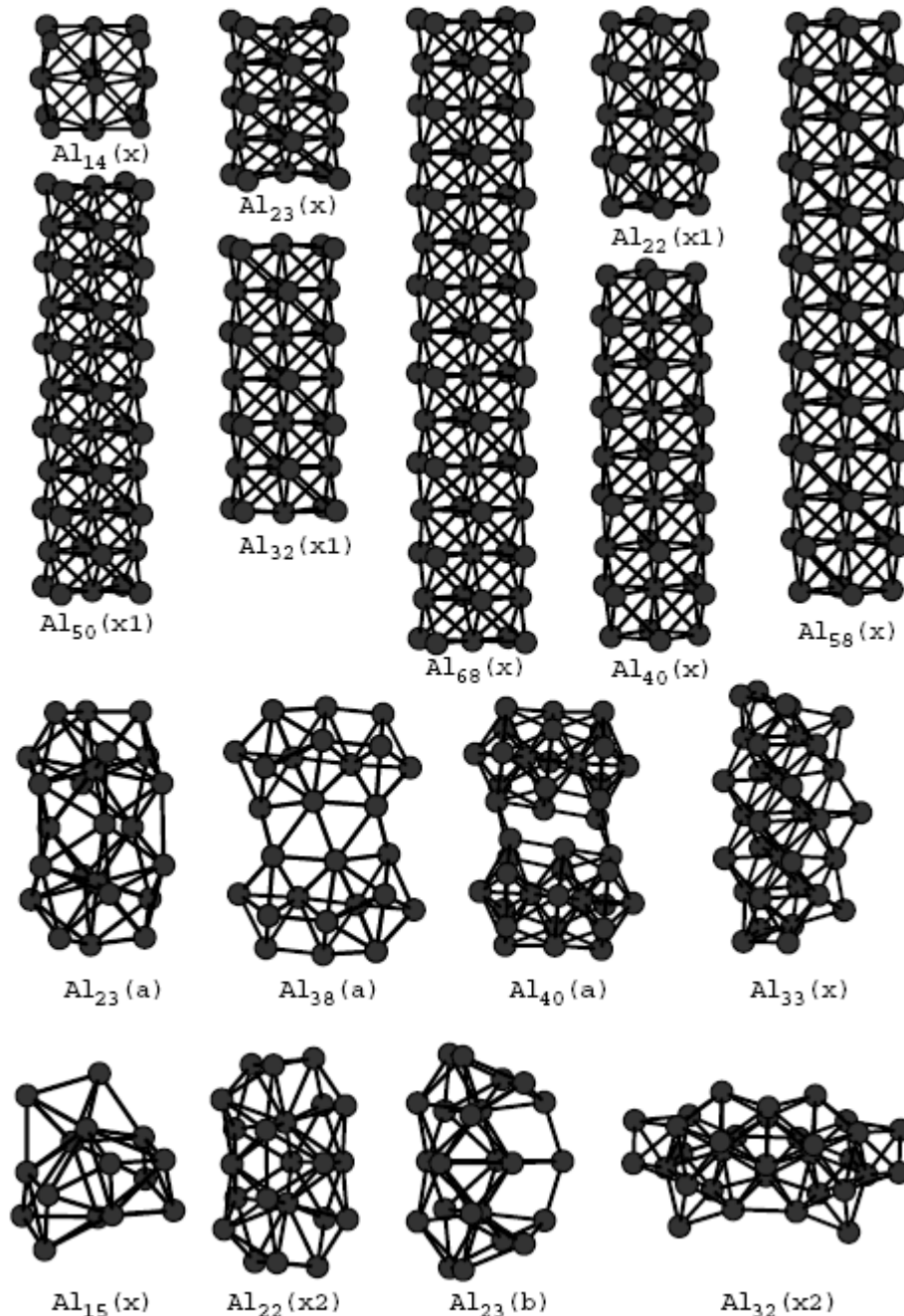


Figure 2. One dimensional stacked structures built on the FCC units, some distorted structures caused by atomic displacement and adsorption and other structures used for comparison.

$\text{Al}_{14}(\text{x})$, $\text{Al}_{22}(\text{x1})$, $\text{Al}_{23}(\text{x})$, $\text{Al}_{32}(\text{x1})$, $\text{Al}_{40}(\text{x})$, $\text{Al}_{50}(\text{x1})$, $\text{Al}_{58}(\text{x})$ and $\text{Al}_{68}(\text{x})$ in figure 2 are all stacked structures from the FCC units. The $\text{Al}_{22}(\text{x1})$, $\text{Al}_{58}(\text{x})$ and $\text{Al}_{68}(\text{x})$ structures misplace a half lattice

constant relative to others. Although the stabilities of the stacked structures are increasing with length, they are all meta-stable structures. In addition, the $\text{Al}_{38}(\text{a})$ and $\text{Al}_{40}(\text{a})$ in figure 2 are stacked by the ground state structures of the Al_{19} and Al_{20} clusters, respectively. But, both of them are not the most stable after being stacked. Here, they are only used for the comparison of structural stability. Their binding energies are listed in Table 1.

Table 1. The binding energies (BE , in eV) of other Al structures.

Struc.	$\text{Al}_{14}(\text{x})$	$\text{Al}_{15}(\text{x})$	$\text{Al}_{22}(\text{x1})$	$\text{Al}_{22}(\text{x2})$	$\text{Al}_{23}(\text{x})$	$\text{Al}_{23}(\text{a})$	$\text{Al}_{23}(\text{b})$
BE	33.92	38.64	57.60	58.97	60.44	63.93	61.15
Struc.	$\text{Al}_{32}(\text{x1})$	$\text{Al}_{32}(\text{x2})$	$\text{Al}_{33}(\text{x})$	$\text{Al}_{38}(\text{a})$	$\text{Al}_{40}(\text{x})$	$\text{Al}_{40}(\text{a})$	$\text{Al}_{50}(\text{x1})$
BE	85.02	88.07	89.30	107.19	109.23	112.96	136.72
Struc.	$\text{Al}_{58}(\text{x})$	$\text{Al}_{68}(\text{x})$	$\text{Al}_{38}(\text{x})$	$\text{Al}_{39}(\text{a})$	$\text{Al}_{39}(\text{b})$	$\text{Al}_{50}(\text{x2})$	$\text{Al}_{63}(\text{x})$
BE	160.56	187.75	108.43	111.00	111.88	141.06	194.55

The shorter stacked structures are easily disturbed, and structural distortion is caused. For example, if an atom in the middle of the $\text{Al}_{32}(\text{x1})$ in figure 2 deviates from its equilibrium position by 0.5 Å, it would bend and transfer into another more stable structure $\text{Al}_{32}(\text{x2})$ as shown in figure 2. The $\text{Al}_{32}(\text{x2})$ lies 3.05 eV higher in energy than $\text{Al}_{32}(\text{x1})$. For a cluster with only 32 atoms, this is a larger energy difference. It is worth noting that the influence of such atomic deviation on the longer stacked structures will decrease. For example, if a middle atom of the $\text{Al}_{50}(\text{x1})$ deviates from its equilibrium position by 0.5 Å, it will go back to its original position. Similarly, after an atom in the middle of the $\text{Al}_{22}(\text{x1})$ in figure 2 deviates from its equilibrium position by 0.5 Å, it would undergo more severe structural distortion into the $\text{Al}_{22}(\text{x2})$. The $\text{Al}_{22}(\text{x2})$ is more 1.37 eV stable than the $\text{Al}_{22}(\text{x1})$. It is also worth noting that two atoms enter the interior of the $\text{Al}_{22}(\text{x2})$ and becomes a compacted structure similar to the $\text{Al}_{23}(\text{a})$.

On the other hand, an Al atom adsorption will also distort its structure obviously. For example, if an Al atom is placed on the middle position of the side surface for the $\text{Al}_{32}(\text{x1})$, it undergoes significant structural distortion into the $\text{Al}_{33}(\text{x})$ in figure 2 after being optimized. Although the $\text{Al}_{33}(\text{x})$ is still not the most stable, its stability is effectively improved due to its distortion. Similarly, the influence is more obvious on the smaller structures. This can be seen from the distortion of $\text{Al}_{14}(\text{x}) + \text{Al}$ to $\text{Al}_{15}(\text{x})$. An atom adsorption increases its binding energy of 4.72 eV. For such a small cluster, this is a large energy difference. This shows that the atomic adsorption makes its stability be greatly improved. Why are the shorter stacked structures more affected? This is because the atomic deviation and adsorption will affect all the atoms in the smaller clusters. But, in the larger or longer clusters, this disturbance affects only its nearby atoms.

Compared to their corresponding ground state structures, the ideal stacked structures built on the FCC units are not very stable. Both atomic displacement and adsorption will almost destroy the small stacked structures. In fact, it is a common phenomenon that an atom is deviated from its equilibrium position or is adsorbed in the deposition process. But, the environmental disturbance makes the ideal stacked structures difficult to exist because their configurations have changed. So, it is reasonable to think that they cannot form during the deposition process on silicone oil surfaces.

The structures $\text{Al}_{38}(\text{x})$, $\text{Al}_{50}(\text{x2})$, and $\text{Al}_{63}(\text{x})$ in figure 3 are also made of the FCC units. They include four, five and eight FCC units, respectively. Their binding energies are also listed in Table I. For the $\text{Al}_{50}(\text{x2})$, four FCC units are connected to the central FCC unit in four directions. The initial structure of the $\text{Al}_{63}(\text{x})$ is a regular octahedron. After being optimized, they exhibit structural distortion. The $\text{Al}_{38}(\text{x})$ is plane-like structure. We have studied the atomic adsorption on it. If an atom is adsorbed on the side and the top surfaces of the $\text{Al}_{38}(\text{x})$ respectively, two stable structures after optimization are obtained. They are shown as the $\text{Al}_{39}(\text{a})$ and $\text{Al}_{39}(\text{b})$ in figure 3. Evidently, the adsorbed atom on the side surface has a great impact on the structure (see $\text{Al}_{39}(\text{a})$). But, the atoms adsorbed on the top surface enter the interior after being optimized and distort the original geometric configuration (see

$\text{Al}_{39}(\text{b})$). The $\text{Al}_{39}(\text{b})$ is more 0.88 eV stable than the $\text{Al}_{39}(\text{a})$, the top atom adsorption has a greater impact on its structure. In the vicinity of the adsorbed atom, both the structures have been obviously distorted.

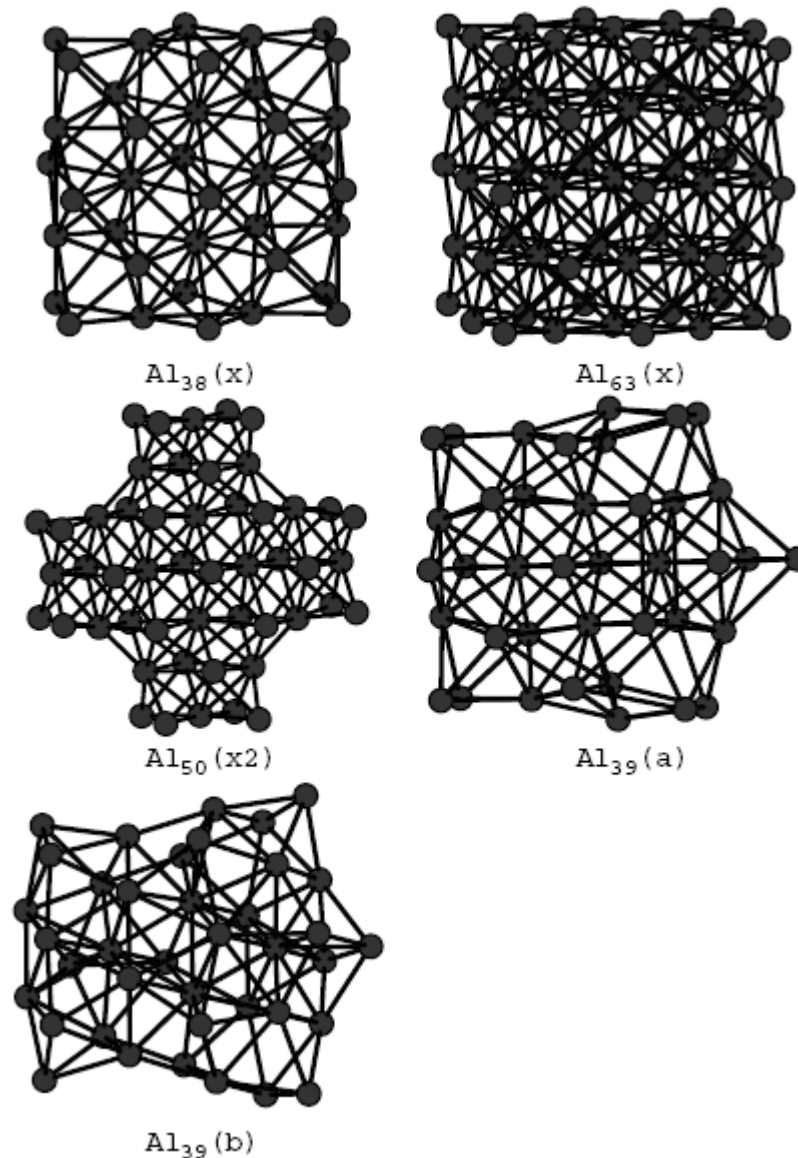


Figure 3. Two and three dimensional stacked structures built on the FCC units, and two distorted structures by an atomic adsorption.

Crystal nucleus is the essential core in the process of crystal growth. On the one hand, the aluminium crystal nucleus is unstable on silicone oil surface. On the other hand, once the initial nuclei are formed, they will also be destroyed by the displacement and adsorption of the atoms.

4. Conclusions

By using the ADF program based on first-principles, we have in detail investigated the structures and aggregates of the small Al clusters. The probability of crystal nucleus formation on silicone oil surfaces is studied. Two conclusions are obtained.

Firstly, two moving Al clusters on liquid substrate meet to form a random structure. Collisions and interactions may make it become a more stable compacted structure. The disc-shaped morphologies would form with deposition due to isotropy on the silicone oil surfaces.

Secondly, the stacked structures from FCC units are not stable. Both atomic displacement and adsorption will have a serious influence on them. They almost destroy the smaller ideal stacked structures from the FCC units. It is thought that it is difficult to form Al crystals on the silicone oil surfaces.

Acknowledgements

This work was supported by the Natural Science Foundation of Zhejiang Province (Grant No. LY16A040011 and LY16A040009), and the National Natural Science Foundation of China (Grant No. 11374082 and No. 11547012).

References

- [1] Kelly K L, Coronado E, Zhao L L, Schatz G C 2003 *J. Phys. Chem. B* **107** 668
- [2] Haus J W, Zhou H S, Honma I, Komiyama H 1993 *Phys. Rev. B* **47** 1359
- [3] Klar T, Perner M, Grosse S, Plessen G Von, Spirkel W, Feldmann J 1998 *Phys. Rev. Lett.* **80** 4249
- [4] Allen N S, Edge M, Ortega A, Liauw C M, Stratton J, McIntyre R B 2002 *Polymer Degradation and Stability* **78** 467
- [5] Storhoff J J, Marla S S, Bao P, Hagenow S, Mehta H, Lucas A, Garimella V, Patno T, Buckingham W, Cork W, Muller U R 2004 *Biosens. Bioelectron* **19** 875
- [6] Son J S, Kim K H, Kwon T Y 2012 *Mater. Lett.* **89** 129
- [7] Giuffrida S, Ventimiglia G, Sortino S 2009 *Chem. Commun.* **27** 4055
- [8] Scirè S, Giuffrida S, Crisafulli C, Riccobene P M, Pistone A 2012 *J. Mol. Catal. A* **353** 87
- [9] Petralia S, Ventimiglia G 2011 *Recent Res. Dev. Photochem, Photobiol* 99
- [10] Ye G X, Michely T, Weidenhof V, Friedrich I, Wuttig M 1998 *Phys. Rev. Lett.* **81** 622
- [11] Torimoto T, Okazaki K, Kiyama T, Hirahara K, Tanaka N, Kuwabata S 2006 *Appl. Phys. Lett.* **89** 243117
- [12] Wender H, Gonçalves R V, Feil A F, Migowski P, Poletto F S, Pohlmann A R, Dupont J, Teixeira S R 2011 *J. Phys. Chem. C* **115** 16362
- [13] Pan Q F, Lv N, Cheng Y, Tao X M, Yang B, Ye G X 2014 *Phil. Mag. Lett.* **94** 29
- [14] Pan Q F, Cheng Y, Tao X M, Yang B, Li B X, Ye G X 2015 *J. Nanopart Res.* **17** 161
- [15] ADF2010.02, SCF, 2010 *Theoretical Chemistry*, Vrije Universiteit: Amsterdam, The Netherlands
- [16] Lenthe E V, Baerends E J 2003 *J. Comput. Chem.* **24**, 1142
- [17] Becke A D 1988 *Phys. Rev. A* **38** 3098
- [18] Perdew J P 1986 *Phys. Rev. B* **33** 8822
- [19] Taylor K J, Pettiette C L, Graycraft M J, Chesnovsky O, Smalley R E 1988 *Chem. Phys. Lett.* **152** 347
- [20] Li X, Wu H, Wang X B, Wang L S 1998 *Phys. Rev. Lett.* **81** 1909
- [21] Schriver K E, Persson J L, Honea E C, Whetten R L 1990 *Phys. Rev. Lett.* **64** 2539
- [22] Fournier R 2007 *J. Chem. Theory Comput.* **3** 921
- [23] Rao B K, Khanna S N, Jena P 1999 *J. Cluster Science* **10** 477
- [24] Kumar V, Bhattacharjee S, Kawazoe Y 2000 *Phys. Rev. B* **61** 8541
- [25] Peng P, Li G F, Zheng C X, Han S C, Liu R S 2006 *Science in China Series E: Technological Sciences* **49** 385
- [26] Yao C H, Song B, Cao P L 2004 *Phys. Rev. B* **70** 195431
- [27] Tian D, Guo X 2005 *Chin. J. Chem. Phys.* **18** 346