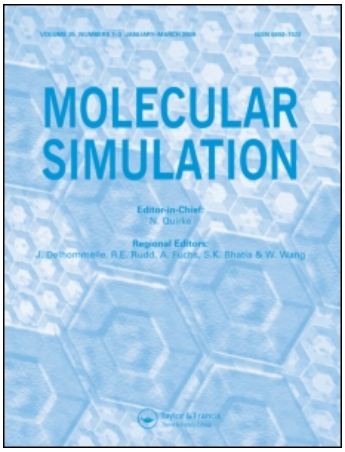

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GRcut: a modeling tool for nanoparticles including five-fold symmetries

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GRcut: a modeling tool for nanoparticles including five-fold symmetries

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A new modeling tool *GRcut* was developed to be used for atomistic simulation of isolated nanoparticles. It generates atomic coordinates in crystalline nanoparticles with equivalent crystallographic surfaces. In addition to 32 crystallographic point groups, nine non-crystallographic point groups with five-fold symmetries are implemented for modeling icosahedral and decahedral clusters in a systematic way. Curved surfaces with spherical, ellipsoidal and cylindrical shapes in arbitrary orientation are also available. This software is useful as a pre-processing tool for molecular simulation on metallic clusters, quantum dots, or fullerenes in high symmetries. The *GRcut* is distributed as a Java applet via the Internet to be used on web browsers.

Keywords: Nanoparticle; Five-fold rotation; Icosahedral cluster; Decahedral cluster; Java applet

1. Introduction

Molecular simulation is widely used in nanotechnology, chemistry and material science. Target materials of simulation are getting to be more complex by increasing computational ability. Not only the solver software of molecular simulation but also the preprocessing environment is important in order to generate computational models systematically. It is sometimes difficult to generate appropriate models including many structural parameters. The present author developed a builder tool *GBstudio* to generate grain boundary models in a systematic way by the $\sum$ value and a few additional parameters. This tool is supplied in a form of Java applet via the Internet [1,2].

The author extended the function of *GBstudio* to generate isolated nanoparticles. In the case of small particles, we must consider not only the crystalline grains but also the pseudo-crystalline ones in icosahedral and decahedral symmetries. Such a modeling tool for nanoparticles including five-fold symmetries does not seem to be supplied for public use. The new software is called *GRcut* (grain-cutter). It generates atomic coordinates in nanoparticles of crystalline and pseudo-crystalline structures in a systematic way. This tool also generates nanoparticles with curved surfaces of spherical, ellipsoidal and cylindrical shapes. *GRcut* is distributed as a Java applet via the Internet [3].

2. Modeling procedures

Let us consider a convex, single crystalline nanoparticle surrounded by crystallographic surfaces. Such nanoparticles are constructed by specifying space group, lattice constants, elements and their asymmetric positions, Miller indices of surfaces and their distance from the center of particle. It is well-known that crystallographic forms are classified into 47 fundamental forms based on 32 point symmetries [4,5]. Polyhedral shape of particle is expressed by a minimal volume surrounded by all equivalent faces with specified distances. Atomic coordinates of nanoparticle are generated by two procedures: (i) calculating the fractional coordinates of atoms in crystalline unit cell by symmetry operations of specified space group, and (ii) listing up the atoms within the minimum volume by stacking the unit cell. Atoms within the surfaces can be assigned by comparing the product of atomic coordinates and the face normal with specified radius. It should be noted that the particle generated in this manner does not preserve its original stoichiometry.

Particles with five-fold symmetries are not described by the 32 crystallographic point groups although they are frequently observed as icosahedral and decahedral clusters [6,7]. Niggli [8] analyzed such non-crystallographic forms

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in icosahedral and general n-fold symmetries. Hahn and Klapper [10] tabulated the non-crystallographic forms of point groups I and I_h. Ino [9] expressed the semi-close packed, icosahedral and decahedral clusters by multiply-twinned particle model (MTP) as combinations of twenty and five subgrains in slightly deformed f.c.c. structures, respectively. In this study, nanoparticles with five-fold symmetries are modeled in a similar way to the MTP model that a particle is composed of single crystal and its replicas. Rhombohedral and monoclinic unit cells with angles of 63.4 and 72° are assumed for icosahedral and decahedral particles, respectively, as shown in figure 1. We do not impose any limitation on the atomic arrangement in the unit cell such as the deformed f.c.c structures in the MTP model. Atomic coordinates in the fundamental single crystal region are generated by the specified point group symmetry and non-negative translations toward a, b and c directions. By using these coordinates, replica atoms are generated by the point group symmetries around the origin.

We consider nine additional point groups with five-fold rotations as I and I_h for icosahedral and C_5, S_{10}, C_{5h}, D_5, C_{5v}, D_{5d} and D_{5h} for decahedral particles [11]. Among them, S_{10} and D_{5d} includes inversion operation which is inconsistent with translation in single crystal. Hence we should care not to extend the single crystal region outside the unit cell in cases of these point groups. Table 1 lists the pseudo-crystaline forms and their Miller indices for nine non-crystallographic point groups. The most fundamental form in I and I_h symmetries, icosahedron, is composed by $\{111\}$. Pentagonal dodecahedron which is another fundamental form is expressed by irrational Miller indices $\{1\ 1/\sqrt{5}\ 1/\sqrt{5}\}$. This means that pentagonal dodecahedron is a mathematical form composed of non-crystallographic surfaces. Other non-crystallographic forms of rhombic triacontahedron and pentakis dodecahedron are expressed by $\{1\ 1\ \tau^{-1}\}$ and $\{h\,k\,(h+k)/2\tau\}$, respectively, where τ is the golden ratio, $(\sqrt{5}+1)/2$. We indicate these indices by $\{1oo\}$, $\{11o\}$ and $\{hko\}$ for convenience where o is a irrational number expressed by other two indices h and k as $(h+k)/2\tau$. Faces $(1oo)$, $(11o)$ and (hko) are perpendicular to [100], [110] and (001), respectively. The face in the lowest symmetry $\{hkl\}$ forms a pentagonal hexahedron and hexakis icosahedron in I and I_h symmetries, respectively. The relations between Miller indices and pseudo-crystalline forms in I and I_h symmetries are resemble to those in O and O_h.

Irrational Miller indices for non-crystallographic forms are also found in decahedral symmetries as $(1o0)$ and (hol) with $o = h/2\tau$. They are perpendicular to [100] and (010), and their equivalent faces form a (di)pentagonal prism and other polyhedra as listed in table 1. The relations between the Miller indices and forms are analogous to those in two-, three- and six-fold point groups. Table 2 shows comparison of notations for equivalent faces used in the present study (GRcut), international tables for crystallography (ITC) [10] and the MTP model [9] in five-fold symmetries. Differences are caused by the axes settings: ITC adopts orthogonal axes of two-fold rotations, and MTP uses the face indices of pre-deformed f.c.c. crystal. Notation in the present study is different from others but is convenient by the analogies to the crystallographic point groups as mentioned above.

3. Software implementation

Modeling procedures in the precedent chapter were implemented in the Java applet *GRcut* with 3D graphics. Two different versions of applet were developed based on plane Java and Java-3D environments. The plain-Java version can deal with relatively large model including about one million atoms. The Java-3D version, on the other hand, is superior in graphic drawing although the maximum size of model is limited up to about 10,000 atoms. Both applets can display the model in three

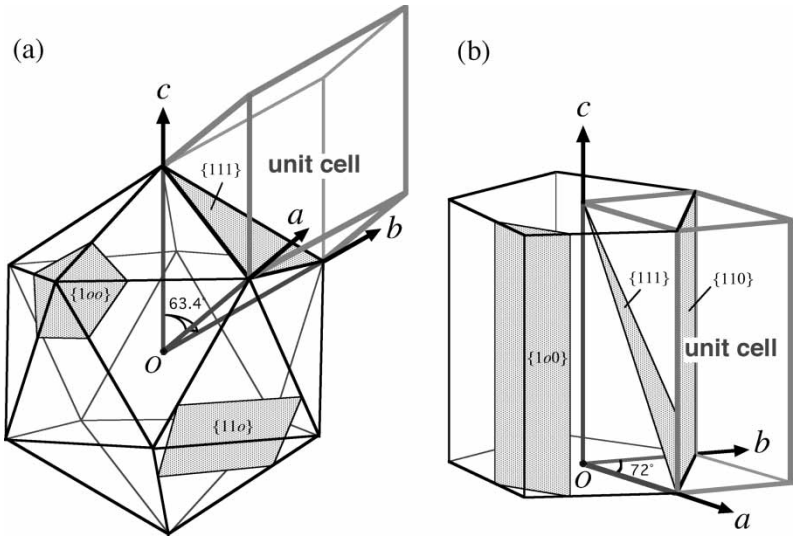

Figure 1. Geometrical settings of unit cells and low-index faces in (a) icosahedral and (b) decahedral symmetries.

Table 1. Pseudo-crystalline forms and the numbers of faces (in parentheses) generated by five-fold point groups.

		I	I_h	
	hkl	Pentagonal hexecontahedron (60)	Hexakis icosahedron (120)	
	hhl	Triakis icosahedron (60), $h > l$ Deltoidal hexecontahedron (60), $h < l$	←	
	hko	Pentakis dodecahedron (60)	←	
	11*o*	Rhombic triacontahedron (30)	←	
	1*oo*	Dodecahedron (12)	←	
	111	Icosahedron (20)	←	
	C_5		S_{10}	C_{5h}
hkl	Pentagonal pyramid (5)		Pentagonal streptohedron† (10)	Pentagonal dipyramid (10)
*hk*0	Pentagonal prism (5)		Decagonal prism (10)	Pentagonal prism (5)
001	Monohedron (1)		Parallelohedron (2)	←
	D_5	C_{5v}	D_{5d}	D_{5h}
hkl	Pentagonal trapezohedron (10)	Dipentagonal pyramid (10)	Dipentagonal scalenohedron (20)	Dipentagonal dipyramid (20)
hol	Pentagonal dipyramid (10)	Pentagonal pyramid (5)	Decagonal dipyramid (20)	Pentagonal dipyramid (10)
hhl	Pentagonal dipyramid (10)	Pentagonal pyramid (5)	Decagonal dipyramid (20)	Pentagonal dipyramid (10)
*hk*0	Dipentagonal prism (10)	←	Didecagonal prism (20)	Dipentagonal prism (10)
1*o*0	Pentagonal prism (5)	←	} Decagonal prism (10)	Pentagonal prism (5)
110	Pentagonal prism (5)	←		Pentagonal prism (5)
001	Parallelohedron (2)	Monohedron (1)	Parallelohedron (2)	←

† Also referred as pentagonal deltohedron or pentagonal trapezohedron.

different ways, *atom* only, *atom & bond* and *bond* only, which are selectable by the buttons.

Geometrical parameters required for modeling are implemented in *Crystal* and *Faces* menus as mentioned below. Examples of nanoparticles as well as crystallographic forms and single crystals can be recalled by the *open* button. After constructing a model, atomic coordinates are displayed by the *Browse* button and can be copied into a local file.

3.1 Crystal menu

Fundamental crystal structures are assigned in the *Crystal* menu. A single crystal is constructed by pressing the *Build* button after specifying space group, lattice constants, elements and their asymmetric positions. Models are generated in a parallelo-hexahedral cell with arbitrary translational vectors, hence this menu can be used as a simple modeling tool of nanoparticles with parallelo-hexahedral shape. Origin of the system is configured at the center of the particle.

Non-crystallographic point groups with five-fold symmetries are implemented in the selection box for space groups. If these point groups are selected, the *Build* button generates a single crystal with rhombic or monoclinic unit cell as shown in figure 1. The generated model does not include five-fold symmetries at this stage.

Table 2. Notations of equivalent faces for icosahedral and decahedral symmetries in the present study (GRcut), ITC [10], and MTP models [9]. See text for definition of o, and τ is the golden ratio, $(\sqrt{5}+1)/2$.

GRcut	*ITC*	*MTP*
(a) Icosahedral		
hkl	*hkl*	–
hhl, $h > l$	0*kl*, $\lvert l/k\rvert < \tau^{-2}$	–
hhl, $h < l$	0*kl*, $\tau^{-2} < \lvert l/k\rvert < \tau$	–
hko	0*kl*, $\lvert l/k\rvert > \tau$	–
11*o*	100	–
1*oo*	01τ	–
111	111	111
(b) Decahedral		
hkl	–	–
hol	–	–
hhl	–	–
*hk*0	–	–
111	–	111
110	–	100
001	–	011

3.2 Face menu

This is the main part of *GRcut* which executes the cutting procedure of nanoparticles with equivalent faces. Figure 2 shows a snapshot of this menu. Candidates of crystal forms are displayed with their Wyckoff letters in the face list box at the middle of the operation pain according to the point group assigned in the *Crystal* menu. Miller indices of desired face, h, k and l, can be assigned by clicking the face list or directly input the numbers. Distance of the face from the origin, hereafter we call it as radius r, is specified in nanometer or the unit of face spacing d_{hkl}. After pressing the *add* button, face indices and radius are registered at the appropriate position in the face list. In the case of figure 2, {100} and {111} faces are registered for *f.c.c.* crystal. Possible particle shapes composed by these faces are truncated cube, cuboctahedron and truncated octahedron. The generated nanoparticle by pressing the *Cut Crystal* button has a cuboctahedral shape since the radii of these faces were selected as 1: 2 in d_{hkl} units.

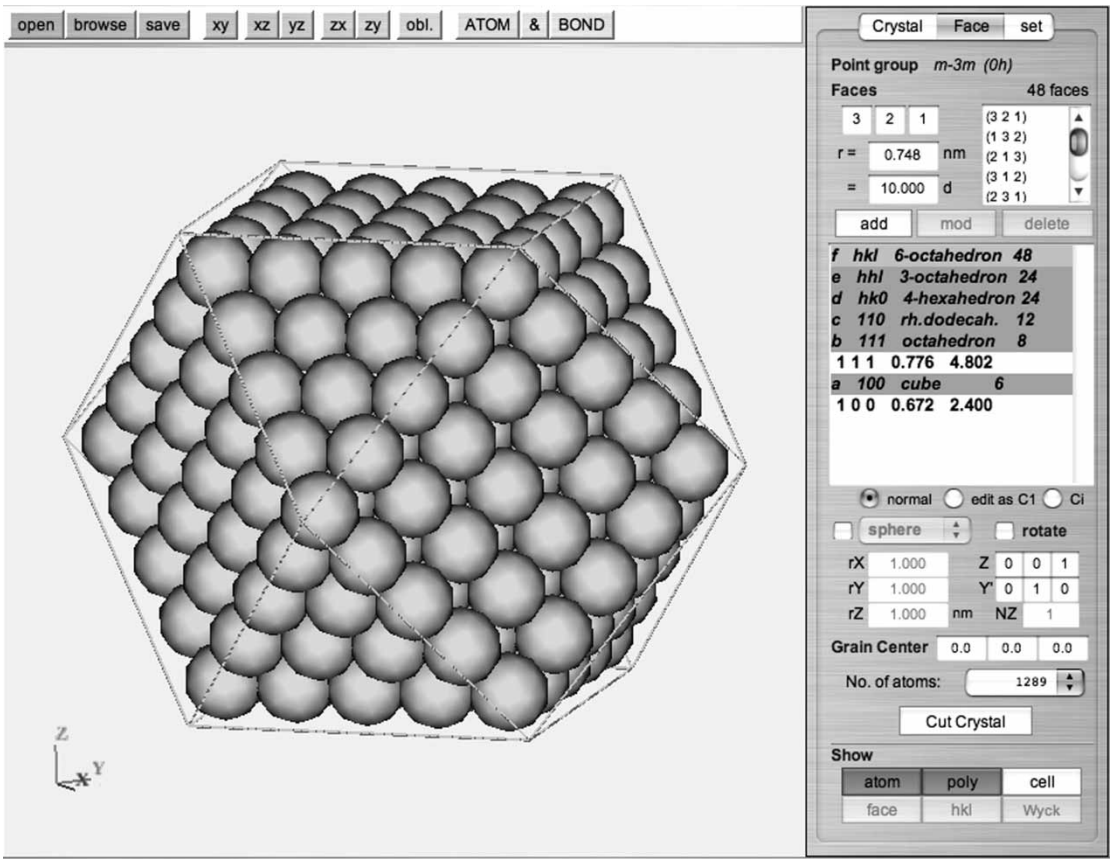

Figure 2. A screenshot of *GRcut*. Constructed model is a f.c.c. cuboctahedron cluster surrounded by {100} and {111} faces.

Complex particle shapes can be generated by adding a number of equivalent faces. Resulted polyhedral shape is displayed in *GRcut* with line drawings based on the algorithm by Kanazawa and Endo [12]. We can expand the equivalent faces $\{hkl\}$ into individual or inversion-symmetric faces by selecting the *Edit as* C_1 or C_i radio button. Anisotropic crystal forms beyond the specified point group are available by using this function. Position of particle center is also addressable by the fractional coordinates in the *Grain Center* input boxes.

The face list and related operation mentioned above are also available for five-fold point groups. The fractional number o is represented by zero in this case. Examples of particle shapes in icosahedral and decahedral symmetries are shown in figure 3 (a)–(d). Figures (a) and (b) are the forms with {111} in both symmetries, and (c) and (d) are the combined forms including irrational Miller indices. Pentagonal faces in (c) and vertically-long hexagonal faces in (d) correspond to $\{1oo\}$ and $\{1o0\}$, respectively.

In addition to the face cuttings, curved surfaces with spherical, ellipsoidal and cylindrical shapes are also available. This option is activated by the checkbox next to the spheroids selection list. Principal radii of spheroids are assigned by *rx*, *ry* and *rz*, and the directions of principal axes, Z and Y', are specified by Miller indices, where Y' is on the Y–Z plane. If the *rotate* checkbox is selected, the model will be rotated so that the principal axes Z and Y' become to be parallel to z axis and y–z plane, respectively. This function operates in the case of ordinary face cuttings. If both cylindrical cutting and rotate option are specified, *GRcut* generates a one-dimensionally periodic model toward z with periodic length Nz. This function is useful for generating nanowire or nanotube models as mentioned below.

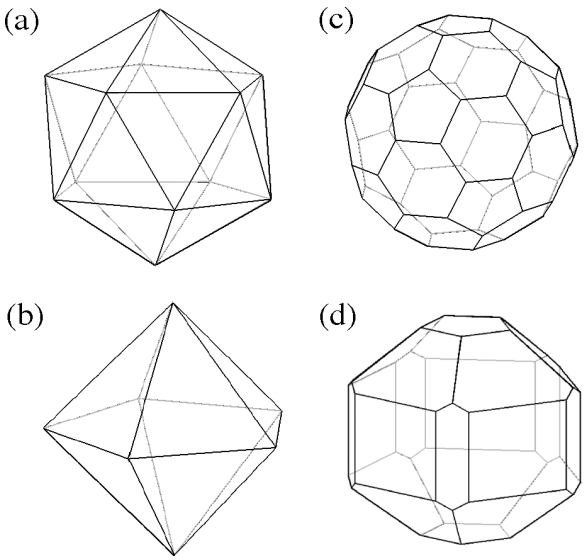

Figure 3. Examples of pseudo-crystalline forms with five-fold symmetries: (a) icosahedron, (b) pentagonal dipyramid, (c) truncated icosahedron and (d) truncated pentagonal dipyramid. Point groups and faces are I_h {111}, D_{5h} {111}, I_h {111} + $\{1oo\}$ and D_{5h} {110} + $\{1o0\}$ + {111} + {001}, respectively.

3.3 Set menu

The *Set* menu is added to change the default settings of *GRcut*. The editable items are atomic color, atomic radius, accuracy of sphere drawing (Java-3D only), axes setting, default view angle and browse format of atomic coordinates. Most of the functions are identical to those in *GBstudio* [1,2].

4. Discussion

Main function of *GRcut* is to generate atomic coordinates of nanoparticles with various surfaces. Physically favorable surfaces are those with lower energies. They are listed, in general, at lower positions in the face list box in the *Face* menu. Combination of different equivalent faces, however, is rather ordinary case [4] because of unstable atoms at the edges or vertices of polyhedron. A spheroidal shape is one solution for eliminating such unstable atoms. In *GRcut*, both types of particle shapes even for the mixture of them is available for the modeling. Generated atomic coordinates can be transferred to other coordinate system by the *rotation* option. These functions are useful for molecular simulation dealing with isolated particles [13].

One of the merits of *GRcut* is that the modeling procedures are completed within one software. Users are free from tiresome calculations of symmetric operation, oblique axes, planner cutting and coordinate conversion. We can concentrate on the particle shape which has a lot of possibilities by combinations of face indices and radii. Another merit of *GRcut* is the applicability to icosahedral and decahedral clusters. Examples of generated nanoparticle models with five-fold symmetries are shown in figure 4. They are the icosahedral and decahedral nanoparticles based on near close-packed structure (a, b), slightly deformed diamond structure (c, d), and graphitic hexagonal pattern (e, f). Models (a) and (b) are well-known icosahedral and decahedral metallic clusters. An icosahedral cluster (a) is generated by only one asymmetric position (000) and face index {111} with arbitrary radius. In the case of decahedral cluster (b), three asymmetric positions (000), (1/2 0 1/2) and (1/2 1/2 0) are required in order to fill up the unit cell in figure 1(b). Equivalent faces specified for model (b) are {110}, {1*o*0} and {111} where {1*o*0} was used to eliminate atoms at the edges of prism planes.

A nanoparticle (c) is a silicon quantum dot Si_{100} expected theoretically [14]. A series of silicon quantum dot including Si_{280}, Si_{600}, Si_{1100}, etc. are modeled by changing the radius of {111} with only two asymmetric positions (*xxx*) and ($x + 1/4$ $x + 1/4$ $x + 1/4$) where $x \approx 0.35$. Model (d) is a silicon nanowire also expected theoretically [15]. In this case, six asymmetric positions are required to fill up the unit cell by diamond-like configuration. Model (d) is different from the theoretical expectation [15] in atomic configuration at the nanowire surface, because energetical relaxation process is not implemented in *GRcut*.

Model (e) shows an example of nested carbon fullerenes. Goldberg type fullerenes expressed by I_h-(5,6) [16] can be modeled by *GRcut* as nesting of fundamental and expanded structures. One asymmetric position (2/3 1/3 0) generates C_{60}, C_{240}, C_{540}, C_{960}, etc. by increasing the radius. Two asymmetric positions (1/3 1/3 1/3) and (2/3 2/3 2/3) produce another series of C_{80}, C_{180}, C_{320}, C_{500}, etc. Non-Goldberg type fullerenes with *I* or I_h symmetry can be also modeled by GRcut as C_{120} I_h-

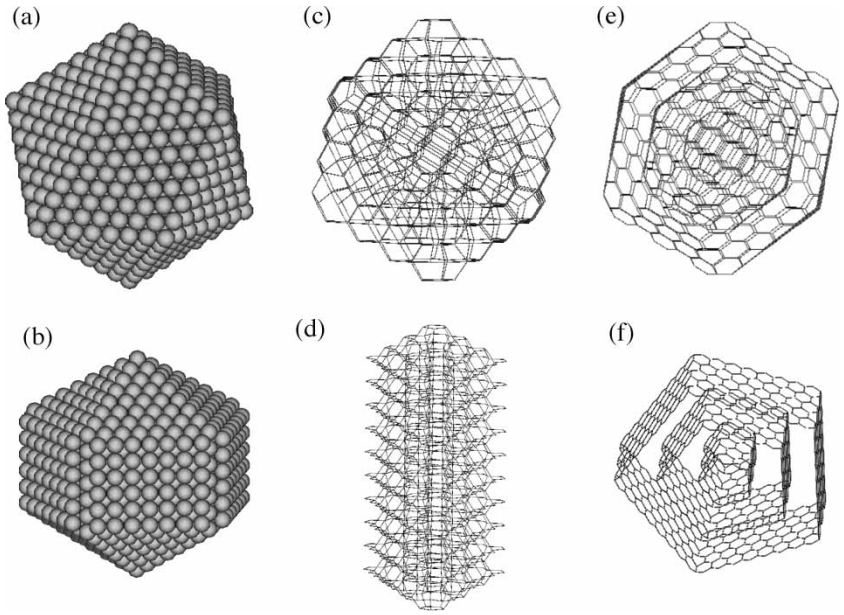

Figure 4. Examples of I_h (icosahedral) and D_{5h} (decahedral) clusters modeled by *GRcut*: (a) M_{1415}, (b) M_{1484}, (c) Si_{600}, (d) silicon nanowire, (e) nesting fullerenes C_{60} @ C_{240} @ C_{540} and (f) nesting carbon nanotubes C(10,0) @ C(25,0) @ C(40,0). Numbers of asymmetric positions are 1, 3, 2, 6, 1 and 4, respectively.

(4,6,10) and C_{480} I_h-(4,6,10,12), for example. The number of asymmetric position is independent on the radius but increases by the chirality. The numbers of asymmetric positions for modeling $C_{140\ L/R}$, $C_{260\ L/R}$ and $C_{380\ L/R}$ of I_h-(5,6) type are three, five and seven, respectively.

Similar discussion is effective for modeling of carbon nanotubes as shown in (f). The resulted model, however, includes unnatural structure parallel to pentagonal prism. Such planner structure can be avoided by adjusting the asymmetric positions, but it leads another problem of ripplings in outer shells. In the case of carbon nanotubes, it is not necessary to use *GRcut* because many specialized software for carbon nanotubes are currently available.

5. Summary

A new modeling tool *GRcut* was developed for generating atomic coordinates in nanoparticle models. It deals with not only the ordinary crystalline particles but also non-crystallographic icosahedral and decahedral clusters in a systematic manner. Spheroidal cuttings with spherical, ellipsoidal and cylindrical shapes are also available. This software may be useful as a pre-processing tool for molecular simulation on metallic clusters, quantum dots, or fullerenes in high symmetries.

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