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Structure of ice Ih and ice Ic as described in the language of Delaunay simplices

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Classification of the Delaunay simplex forms is carried out for the ideal structures of ice Ih and ice Ic. Classification according to the number of edges of different length reveals six types of simplices, while classification according to the number and mutual positions of edges of the unit length (equal to the length of the hydrogen bond) reveals five types of indices. Ice Ic is composed of simplices of three types (one of which has the form of a perfect tetrahedron), ice Ih from six simplices. Degeneracy is removed in computer models of slightly distorted ice by means of insignificant shifting of water molecules from their ideal positions. This makes it possible to provide the unambiguous partition of the crystal structure into Delaunay simplices. It is found that degeneracy removal results in the appearance of Delaunay simplices of specific forms with a very small volume (Kije simplices). The shape characteristics of simplices of different types and their percentage are calculated in the large computer models of ice. In particular, the fraction of the Kije simplices is found to be about 7.5% in ice Ih.

1. Introduction

Geometric Voronoi–Delaunay methods provide a very effective tool to analyse the structure of computer models of molecular systems. The advantages of these methods lie in the possibility of partitioning the space of the model into simple geometric objects in a mathematically strong and unambiguous way. The first of these objects, the Voronoi polyhedron (VP), corresponds to each atom of the system and characterizes the space region that is nearest to its centre. Two atoms sharing a VP face are the nearest, geometric neighbours. One uses the VP for studying the local atom environment, for example, its local density. The second object, the Delaunay simplex (DS), describes, in contrast, the space between the atoms. Each DS is a tetrahedron whose vertices are the centres of the four atoms that are the geometric neighbours of each other; it corresponds unambiguously to an empty interstitial sphere inscribed between these atoms. The size of interstitial spheres, the volume, form and arrangement of the Delaunay simplices make it possible to describe the structure of empty interatomic space. Detailed information about the properties of the VP and DS can be found in Rogers (1964), Medvedev (2000), Okabe *et al.* (2000).

Thus far the Voronoi–Delaunay method has been used to describe the structures of various models from the packing of hard spheres to aqueous solutions of complex biological molecules. Voronoi polyhedron language has found wide use whereas that of the Delaunay simplex is less common, despite the fact that it is extremely effective for describing the structure of the dense irregular packing of atoms in simple liquids. As is known (see, *e.g.*, Kelly & Groves, 1970), in the crystal closest packings of spheres there are two types of interstitial voids: tetrahedral and octahedral ones. A tetrahedral configuration of four atoms forming the void of the first type is a Delaunay simplex. An octahedral configuration of six atoms forming the void of the second type is nonsimplicial and can be divided into four simplices in the form of one-fourth of an octahedron (quartoctahedron) when displacing slightly atom positions relative to the coordinates of a perfect octahedron. Thus, the structure of f.c.c. (face-centred cubic) and h.c.p. (hexagonal close-packed) crystals can be partitioned into the two kinds of Delaunay simplices, the number of quartoctahedra being twice as much as that of the tetrahedra. Advancing to applying the Delaunay simplices to describe simple liquids (consisting of spherical atoms) is explained by the fact that the basic structural elements of these systems are the same simplex types as in closest-packed crystals, *i.e.* tetrahedra and quartoctahedra (Naberukhin *et al.*, 1991; Naberukhin & Voloshin, 2006). However, the fraction of tetrahedra in irregular packings is considerably greater and their arrangement is principally different than in crystals: tetrahedra in liquids are organized in long branched chains which permeate the whole volume of the specimen.

Voronoi polyhedron language is also used extensively for studying the structure of water. In contrast, Delaunay simplices in water and aqueous systems have been investigated little. We know of only two papers (Tytik, 2008*a*,*b*) in which the author considers some properties of Delaunay partitioning in the ices Ih and Ic, but does not give the full classification of Delaunay simplices. Disregard of DS in water

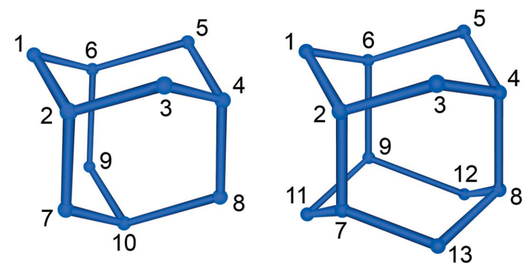

Figure 1
Modules of the ice structures: left, ice Ic; right, ice Ih. Coordinates of the water molecule centres: 1 ($-2a$,0,0); 2 ($-a$,$-b$,$-c$); 3 (a,$-b$,$-c$); 4 ($2a$,0,$-c$); 5 (a,b,0); 6 ($-a$,b,$-c$); 7 ($-a$,$-b$,$-4c$); 8 ($2a$,0,$-4c$); 9 ($-a$,b,$-4c$); 10 (0,0,$-5c$); 11 ($-2a$,0,$-5c$); 12 (a,b,$-5c$); 13 (a,$-b$,$-5c$). $a = (2)^{1/2}/3$; $b = (2/3)^{1/2}$; $c = 1/3$. Length unit is equal to the distance between oxygen atoms of neighbouring water molecules.

and ice can be explained by the absence of prevailing forms of Delaunay simplices in the loose-packed systems, particularly in water: here a wide variety of their forms exists for which the principles of classification have still not been devised. It is reasonable to begin the investigation with an analysis of the ice structures. In the present work we carry out a classification of Delaunay simplices for the structures of ordinary hexagonal ice (ice Ih) and metastable cubic ice (ice Ic). All hydrogen bonds in these ices are directed at tetrahedral angles (see Wyckoff, 1963), so that they represent two variants of the perfect tetrahedral network of hydrogen bonds.

2. Structure of ice Ih and ice Ic

For our aim to classify the Delaunay simplices it is convenient to represent the ice structure not by the unit cell of a crystallographic lattice but by the *module* – a specific group of molecules which, being attached one to another, makes it possible to describe the whole of the crystal structure. These modules are depicted in Fig. 1 where sites correspond to the centres of molecules, *i.e.* to the centres of oxygen atoms.

Modules may be imagined as 'baskets' at the faces of which hexagonal rings are situated (Fig. 2). A basket of ice Ic represents a perfect tetrahedron (points 2, 4, 6 and 10) whose edge length is equal to the distance between second neighbours of water molecules along the hydrogen bonds (this distance we designate as $R2$). A basket of ice Ih is a triangular prism (points 2, 4, 6, 7, 8 and 9). In ice Ic the ring of chair form

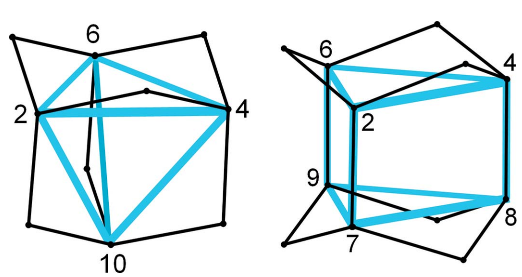

Figure 2
Module baskets (shown in blue): left, ice Ic (perfect tetrahedron); right, ice Ih (triangular prism).

is situated at each face of the basket whereas in ice Ih rings–chairs are situated only at the triangular bases of the prism and the rings of boat form are placed at its rectangular faces. The sites of the rings are vertices of some polyhedra which we name ring polyhedra. The module polyhedron is comprised of the basket together with adjacent ring polyhedra. (It should be noted that module polyhedra are not stereohedra since the ring polyhedra are common parts of two adjacent module polyhedra. This is of no importance for our aim as we are interested in revealing all forms of DS but not in the problem of partition of space into equal polyhedra.)

All six molecule centres forming the rings are placed on the same sphere whose interior does not contain other centres of the crystal structure. The centre of this sphere is simultaneously the centre of an interstitial sphere which can be inscribed between six molecules forming the ring. Interstitial spheres of another type are situated in the centres of spheres circumscribed around baskets. All types of interstitial spheres of module polyhedra are presented in Fig. 3. They overlap one another and illustrate a peculiar picture of empty space in the ice.

Itoh *et al.* (1996) distinguished two types of interstices in ice Ih designated as Tu (uncapped trigonal) and Tc (capped

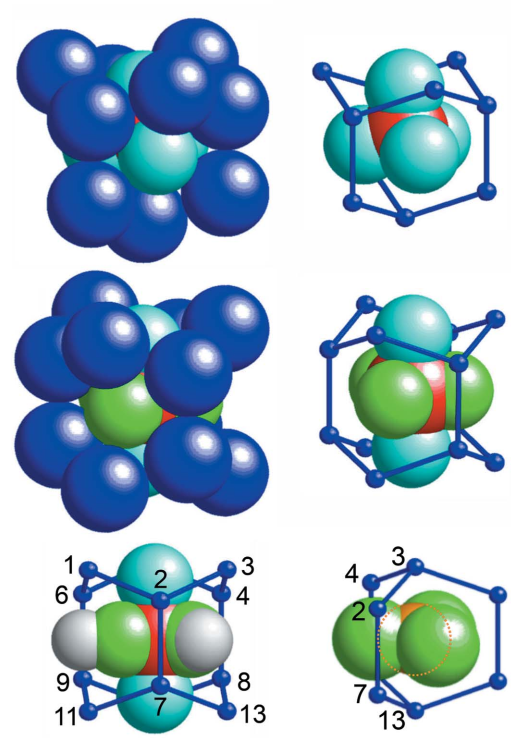

Figure 3
Arrangement of the interstitial spheres relative to water molecules. Top row – ice Ic, middle and bottom rows – ice Ih. Blue spheres with radius 0.5 correspond to water molecules (on the right their radius is diminished fivefold for clarity). Interstitial spheres of the chair ring are given in cyan, spheres of the boat ring in green, spheres of the baskets in red. Grey spheres show interstitial spheres of the Kije trapezoids (left sphere corresponds to the trapezoid 1, 6, 9, 11, right sphere to trapezoid 2, 3, 13, 7). Right picture of the bottom row depicts the so-called capped trigonal site (Tc) where a central void sphere (with radius 5/6) is given in orange.

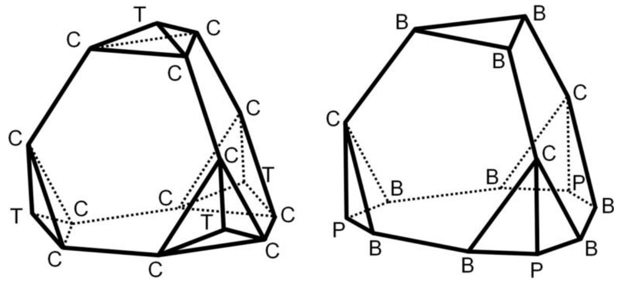

Figure 4
Voronoi polyhedra in ice Ic (left) and ice Ih (right). C – centres of the chair rings, B – centres of the boat rings, T – centres of the tetrahedron baskets, P – centres of the prism baskets.

trigonal) sites. A Tu site is equivalent to the centre of our basket prism. A Tc site is the centre of a configuration formed by three adjacent boat rings (see Fig. 3, bottom right). It is unreasonable to designate a Tc site as an interstice because it is bounded by only two water centres ('caps', numbers 3 and 13 in Fig. 3), whereas a true interstitial sphere is bounded by four or more centres. It is self-evident that an interstitial water molecule, being introduced into a Tc site, cannot remain here and will move towards the adjacent Tu site or interstices of rings; the authors did observe this situation by molecular dynamics simulation.

As is known, the centres of interstitial spheres, coinciding with the centres of the circumspheres of Delaunay simplices, are the vertices of the Voronoi polyhedra. Such polyhedra for two forms of ice are presented in Fig. 4.

3. Classification of the Delaunay simplices in the structures of ice Ih and ice Ic

Partitioning the module polyhedra into Delaunay simplices involves the constituent DS of the ring polyhedra and the DS of the basket. All six sites of each ring, both chair and boat, are situated on the same circumsphere whose centre coincides with the centre of the ring and whose radius is $R_{\rm ring} = (33/36)^{1/2}$. Inside of this sphere there are no other centres of molecules of the crystal; therefore we may conclude, according to the Delaunay theorem on the empty sphere (see Delaunay, 1934; Medvedev, 2000), that all tetrahedra into which ring polyhedra can be partitioned are Delaunay simplices. Because the number of molecules situated on the circumsphere is more than four, the ring configurations of molecules are degenerate, *i.e.* they can be partitioned into DS in a variety of ways. All sites of baskets are situated on one circumsphere, too, and inside of it there are no other sites of the module polyhedron. A basket of ice Ic, being the perfect tetrahedron, is a single Delaunay simplex. The molecular configuration of the basket prism of ice Ih is degenerate and can be divided into several simplices. The possible variants of partitioning the module polyhedra into DS in the ideal structures of ice can be found by simple examination of options. These variants are displayed in Fig. 5 for ring polyhedra and in Fig. 6 for basket ones.

Table 1
Classification of Delaunay simplices according to edge lengths.

$R1 = 1$	Distance between oxygen atoms of nearest molecules (length of the hydrogen bond)
$R2 = (8/3)^{1/2} = 1.6330$	Distance between next nearest molecules across the ring
$R3 = (11/3)^{1/2} = 1.9149$	Distance between molecules disposed at diametrically opposite vertices of the chair ring
$R3\text{bis} = 5/3 = 1.6667$	Distance between molecules disposed at upper vertices (bow and poop) of the boat

Simplex type	Edge composition
Type I	$2R1 + 3R2 + R3$
Type Ibis	$2R1 + 3R2 + R3\text{bis}$
Type II	$3R1 + 2R2 + R3$
Type III	$2R1 + 2R2 + R3 + R3\text{bis}$
Type IV	$R1 + 3R2 + 2R3$
Type V	$R1 + 2R2 + 3R3$
Kije rectangle	$2R1 + 2R2 + 2R3$
Kije trapezoid	$3R1 + 2R2 + R3\text{bis}$

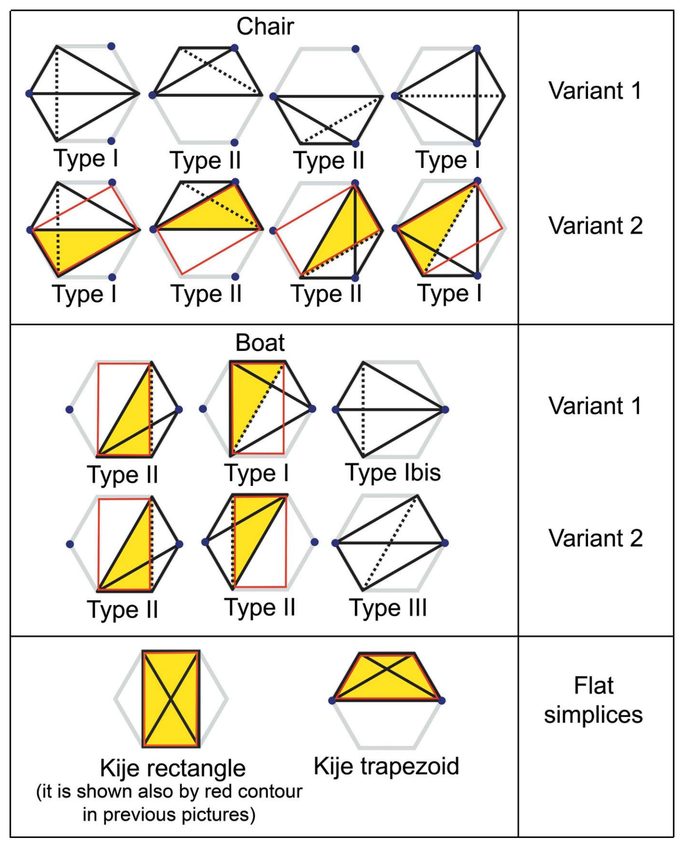

Figure 5
Delaunay simplices of ring polyhedra. Grey rings depict the projections of rings on a plane normal to their axis. Black points correspond to vertices lying above a plane in which other vertices are situated. The projections of Delaunay simplices are shown by black lines; the invisible edges (situated behind the simplex body) are shown by a black dotted line. Filling the space of a ring polyhedron will be fulfilled when superimposing successively one simplex on another beginning with the extreme left simplex in each variant. Coloured details are explained in the text.

Table 2
Properties of the Delaunay simplices in nearly ideal ice Ih.

123200 sites from 35 × 20 × 22 unit cells. 1064916 Delaunay simplices. Fractions of DS edges: $R1$ 20.73%; $R2$ 51.04%; $R3$bis 5.18%; $R3$ 23.05%.

Index and total fraction	Fraction (for ideal ice in parentheses)	Circumradius	Volume	Tetrahedricity measure	Simplex type
1 0.173535	0.11569 (1/8)	$R_{\rm bask}$	0.38490	0.08501	Type IV
	0.05785 (1/16)			0.09074	Type V
2 0.098053	0.07235 (5/64)	$R_{\rm ring}$	0.21383	0.13454	Type III
	0.02570 (0)		3.82×10^{-5}	0.15283	Kije rectangle
3 0.318065	0.10118 (7/64)	$R_{\rm ring}$	0.21383	0.10782	Type I bis
	0.21687 (15/64)		0.12830	0.13335	Type I
5 0.410348	0.04878 (0)	$R_{\rm trap}$	3.06×10^{-5}	0.14263	Kije trapezoid
	0.36158 (25/64)	$R_{\rm ring}$	0.12830	0.18194	Type II

$R_{\rm ring} = (33/36)^{1/2} = 0.95740$, circumradius of rings. $R_{\rm bask} = (41/36)^{1/2} = 1.06715$, circumradius of basket prism. $R_{\rm trap} = (3/4)^{1/2} = 0.86604$, circumradius of the Kije trapezoid.

Table 3
Properties of the Delaunay simplices in nearly ideal ice Ic.

125000 sites from 25^3 unit cells. 1125750 Delaunay simplices. Fractions of DS edges: $R1$ 19.98%; $R2$ 59.97%; $R3$ 20.05%.

Index	Fraction (for ideal ice in parentheses)	Circumradius	Volume	Tetrahedricity measure	Simplex type
0	0.11104 (1/9)	$R1$	0.51320	0.0000	Basket tetrahedron
2	0.00067 (0)	$R_{\rm ring}$	3.02×10^{-5}	0.15283	Kije rectangle
3	0.44415 (4/9)	$R_{\rm ring}$	0.12830	0.13335	Type I
5	0.44415 (4/9)	$R_{\rm ring}$	0.12830	0.18194	Type II

Fig. 5 shows that ring polyhedra can be broken up into four and three DS for the ring–chair and the ring–boat, respectively, with two variants of partitioning in both cases. The ring–chair polyhedron is made up of the simplices of two types which can be classified by the numbers of edges of different length; this classification is given in Table 1. In the ring–boat polyhedron two additional types of simplices exist, the type Ibis differing from type I only by the length of the longest edge. The basket polyhedron of ice Ic is the Delaunay simplex in the form of a perfect tetrahedron, whereas in ice Ih it is divided into three simplices of two types (Fig. 6).

We performed a computer analysis of ice models to corroborate the partitions found 'theoretically' and to determine the statistics of different variants. The ideal forms of ice were slightly disturbed by shifting the positions of molecules one by one and completely at random within a sphere of radius 10^{-4} of hydrogen-bond length. Such a distortion of coordinates is sufficient to remove the degeneracy, *i.e.* to exclude an ambiguity of partitioning the nonsimplicial polyhedra and to ascribe to each simplex its own separate circumsphere. All results of computer analysis are summarized in Tables 2 and 3. They reveal unexpected and nontrivial facts.

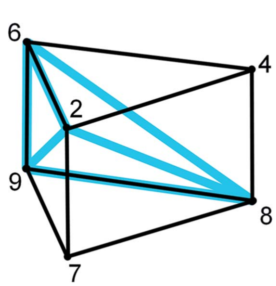

Figure 6
Delaunay simplices of the basket of ice Ih. Blue lines mark a simplex of the type V: $R1 + 2R2 + 3R3$. Simplices of the type IV ($R1 + 3R2 + 2R3$) are placed on the top and on the bottom relative to it.

The most nontrivial result of the partition of the module polyhedra into Delaunay simplices after degeneracy removal is the appearance of simplices of a specific form with nearly zero volume (see Tables 2 and 3). Simplices of such a kind were first discovered by us in the model of Lennard-Jones liquid and have been named the Kije simplices (Voloshin *et al.*, 1989); such simplices appear of necessity in the structure of simple liquids and are their characteristic property (Naberukhin & Voloshin, 2006). Kije simplices arise when, in a polyhedron analysed, there are four vertices lying in the same plane; it makes no difference whether they compose a face of some polyhedron (as points 2, 4, 7 and 8 in the boat in Fig. 1) or not (as points 1, 2, 4 and 5 in the chair). After degeneracy removal these four vertices leave the plane and form a flat tetrahedron with a very small volume. If the circumsphere of this tetrahedron does not contain other sites of the given or neighbouring module polyhedra, so this tetrahedron is, by definition, a Delaunay simplex and we designate it as the Kije simplex. Otherwise these vertices compose four triangles which are components of other simplices into which a module polyhedron is partitioned.

The possible variants of appearance of the Kije simplices are presented in Fig. 5 outlined in red. The ring–boat polyhedron is situated on the rectangular face of the ice Ih basket. In the ideal crystal two triangular faces of adjacent simplices of the ring (coloured yellow in the figure) compose a plane rectangle which coincides with the basket face. Two diagonals of this rectangle may not coincide after degeneracy removal, resulting in the Kije simplex (if its circumsphere does not contain other sites of the system). Such a possibility exists in both variants of the partition of the ring–boat. The ring–boat polyhedron has other plane tetragonal faces in the form of a trapezoid by which neighbouring module polyhedra are joined. Two diagonals of this trapezoid may not coincide in adjacent modules after degeneracy removal; then a trapezoid may transform to the Kije simplex of negligible volume. In Fig. 3 (left picture of the bottom row) an actual case of degeneracy removal is displayed when two Kije trapezoids occur together with corresponding interstitial spheres.

The ring–chair polyhedron has no completed plane rectangular face, but a plane rectangle (outlined in red in Fig. 5) is composed of four triangular faces of four simplices into which the ring is partitioned in variant 2 – they are coloured yellow in Fig. 5. Fig. 5 displays a case when two diagonals of the rectangle do not lie in the same plane in two pairs of simplices after degeneracy removal; this may result in the appearance of a Kije simplex (if the circumsphere of the distorted rectangle does not contain other sites of the system).

Tables 2 and 3 give the characteristics of all Delaunay simplices found in the computer models of slightly distorted forms of ice Ih and ice Ic. In addition to classification of simplices according to the types given in Table 1, here we also indicate the classification according to *simplex index*, that is, the sum of the number of edges with length $R1 = 1$ plus the number of sites in which two or more edges of such a length meet. We see that in the almost ideal ices only five types of indices among ten possible variants are realized, with only four types in each ice. The tables present the fractions of each type of Delaunay simplex found in the models. In addition, the tables indicate the radius of the circumsphere, simplex volume and characteristics of its shape – the tetrahedricity measure T which is proportional to the dispersion of lengths l_i of all its edges normalized to mean square length:

$$T = \sum_{i>k} (l_i - l_k)^2 / 15\langle l \rangle^2.$$

For a perfect tetrahedron $T = 0$ (see DS with index 0 in Table 3).

It should be noted that the total fraction of Kije simplices (rectangles and trapezoids) in ice Ih amounts to 7.5%, *i.e.* these types of simplices can in no way be neglected among all simplices. In ice Ic the fraction of Kije simplices is two orders smaller. Another method of degeneracy removal may lead to different values for the simplex fractions (especially for Kije simplices); however these differences will be minor.

4. Conclusions

We carried out a classification of the Delaunay simplex forms in the ideal structures of hexagonal (ice Ih) and cubic (ice Ic) ice. Classification according to the number of edges of different length reveals six types of simplices, while classification according to the number and mutual positions of edges of the unit length (equal to the length of the hydrogen bond) reveals five types of indices. Ice Ic is composed of simplices of three types (one of which has the form of a perfect tetrahedron), and ice Ih from six simplex types. Degeneracy, *i.e.* a situation when more than four sites of the crystal lattice are situated on the empty simplex circumsphere, is removed in computer models of slightly distorted ice by means of insignificant shifting of water molecules from their ideal positions. This offers the possibility of providing the unambiguous partition of the crystal structure into Delaunay simplices. It is found that degeneracy removal results in the appearance of Delaunay simplices of specific forms with very small volume (Kije simplices) which arise when in an ideal lattice there are four sites lying in the same plane. The shape characteristics of simplices of different types and their percentage are calculated in the large computer models of ice. In particular, the fraction of the Kije simplices (of two types) is found to be about 7.5% in ice Ih.

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