

**Structure analysis methods for crystalline solids and supercooled liquids**

Da-Qi Yu, Min Chen,\* and Xiu-Jun Han

*Department of Engineering Mechanics, Tsinghua University, Beijing 100084, People's Republic of China*

(Received 30 March 2005; revised manuscript received 23 June 2005; published 14 November 2005)

The three most widely used methods for analyzing atomic structures are evaluated by simulating crystalline solids and supercooled liquids. The local order parameter approach due to Volkov *et al.* [Phys. Rev. E **66**, 061401 (2002)] fails in randomly perturbed body-centered-cubic environments, while the pair analysis method behaves as an approximate approach depending on how the neighborhood is defined. As to the Voronoi analysis method, we improve the procedure of Brostow *et al.* [Phys. Rev. B **57**, 13448 (1998)] to eliminate distorted Voronoi faces and edges which originate from thermal vibrations and computational rounding errors. The improved procedure works robustly in face-centered-cubic, body-centered-cubic, and hexagonal close-packed environments. When the pair analysis technique and the Voronoi analysis method are applied to detect the microstructure and its evolution in supercooled liquids, qualitatively consistent results are attained.

DOI: [10.1103/PhysRevE.72.051202](https://doi.org/10.1103/PhysRevE.72.051202)

PACS number(s): 61.20.Ja, 61.20.Ne, 64.70.Dv

**I. INTRODUCTION**

Nucleation and glass transition in supercooled liquids have been actively studied by computer simulations and experiments [1–8]. However, there remain many open questions on the detailed knowledge of the microscopic structure and its evolution in supercooled liquids, whether for monatomic model systems such as Lennard-Jones (LJ) fluids [3–6] or for much practical systems such as colloids [7–11], liquid metals, and alloys [12–17]. In the structure analysis process of those computer-simulated or experimentally prepared materials, a robust analysis method is believed to be the key to achieve reliable results [2–5,8,10,11,13].

Methods using local bond-orientational order parameters [5,18] have gained increasing interests [5–8,11]. In the original method of ten Wolde *et al.* [5,6], structure components are attained by comparing the distributions of local order parameters between the interested cluster and typical equilibrium structures, such as face-centered-cubic (fcc), hexagonal close-packed (hcp), body-centered-cubic (bcc), icosahedral (ico) environments, and so on [5–8]. Another version of this method was given by Volkov *et al.*, who compared the local order parameters of perfect structures with the corresponding ones of each atom in the studied materials [11]. This approach avoids the difficulties in preparing typical quasiequilibrium structures, but has not been widely validated even in equilibrium crystalline solids.

There are alternative approaches to analyze microstructures based on the operation of graphs. One is the pair analysis technique first introduced by Andersen and co-workers [3,19]. In this method, pair indices are given for each pair of atoms in order to describe the neighborhood of this pair. Though is favored as a common technique for analyzing pair structures [13–17,19–21]; this approach is not able to identify which structure does a particular atom belong to, in supercooled liquids. Furthermore, the dependence of pair indi-

ces on the definition of neighboring atoms has not been estimated.

A more complicated approach is the Voronoi analysis method [4,10,22–24], which was first used by Finney as early as 1970 [22]. For each particle, an associated Voronoi polyhedron is created, whose shape characterizes the local structure. Unfortunately, there are vertices where four faces meet in the Voronoi polyhedron in fcc and hcp environments. These vertices are unstable and often split into small faces or edges because of thermal fluctuations and rounding errors in computation. Then the Voronoi polyhedron is distorted. Physicists used to eliminate all the edges shorter than a threshold value to reduce this distortion [4,23]. However, for crystals at higher temperatures relevant to supercooled liquids, the faces and edges resulting from thermal vibrations may be comparable to the original ones, and it is not very reasonable to eliminate all edges shorter than a single threshold value. To overcome this difficulty, Brostow *et al.* proposed an iteration process to choose a particular value for each Voronoi polyhedron [24]. Their approach seems to be efficient in moderately perturbed fcc and hcp lattices [24], but has not been tested in perturbed bcc lattices and equilibrium fcc and hcp lattices at higher temperatures.

In the present work, we examine the above-mentioned methods by simulating bcc, fcc, and hcp lattices and supercooled liquids. The local order parameter method due to Volkov *et al.* [11] is shown to mistake atoms in randomly perturbed bcc environments for hcp or fcc structures. The dependence of pair indices on the definition of neighboring atoms in the pair analysis method is evaluated at different temperatures. By analyzing the characteristics of Voronoi faces and edges, we have further modified the Voronoi face and edge elimination process. Results are compared when the last two methods are applied to analyze the microstructure and its evolution in supercooled liquids.

**II. STRUCTURE ANALYSIS METHODS****A. Portrayal of the systems**

The simulation systems are generated by placing 32 000 and 34 992 atoms in perfect fcc and hcp lattices, respectively.

---

\*FAX: +86-10-62781610. Electronic address: mchen@tsinghua.edu.cn

The particles are interacted with each other by a so-called shifted LJ potential [4,19], in which the conventional LJ potential is truncated to zero for distances larger than 2.5 in reduced LJ units and shifted upward by the potential value at this distance. The units of all quantities are conventionally reduced. *NVT* ensemble molecular-dynamics (MD) simulations of constraint method [25,26] are performed at reduced temperature  $T^*=0.6$  and density  $\rho^*=0.95$  in cubic with periodic boundary conditions. The equations of motion are integrated by the velocity Verlet scheme [27] with a time step  $\Delta t^*=0.005$ .

After equilibrium, coordinates of particles are recorded for further analysis and the distributions of atomic displacements are calculated. An identical Gaussian form is shared by all the distributions of atomic displacements in three dimensions for both equilibrium fcc and hcp lattices. In order to collect the information in the bcc environment, which lacks mechanical stability in the LJ system, we use the Gaussian distribution to perturb the perfect bcc lattice.

In order to prepare a metastable liquid, the fcc lattice is heated and equilibrated to a temperature as high as  $T^*=1.2$ . Then the system is cooled and relaxed to  $T^*=0.6$ . The radial distribution function (RDF) is checked to be of typical liquid character in each situation.

### B. Local order parameter method

The local order parameter method devised by ten Wolde *et al.* [5,6] starts from a definition of neighbors or bonds for each atom  $i$ , by choosing all particles  $j$  within a given radius  $r_q$  from  $i$ . According to the bond-orientational order parameters proposed by Steinhardt and co-workers [18], ten Wolde *et al.* constructed a series of local order parameters  $q_l(i)$  and  $w_l(i)$  [5]. For any interested cluster, the distributions of local order parameters  $q_l(i)$  and  $w_l(i)$  are measured and fitted to those of typical equilibrium structures, in order to calculate the structure components of the cluster [5–8].

Generally, the distributions of local order parameters for metastable structures, which have been proved to be ultraimportant in supercooled liquids, are not easy to be gathered [7]. This is because of the difficulties in generating bulk long-lived metastable systems. Moreover, the distributions of local order parameters may be too rough to fit in tiny clusters, which become more important in highly supercooled liquids [4]. An alternative approach was given by Volkov *et al.* [11]. In their method, the local order parameters  $q_l(i)$  and  $w_l(i)$  of perfect structures are employed to fit the corresponding ones of each atom in the studied configurations. Then the atom is assigned to the structure with the biggest component.

However, we find that this alternative approach could be very dangerous. As shown in Fig. 1, though they have distinct differences, the distributions of local order parameters from different structures intersect with each other. Similar behavior was presented in the experiment of colloidal crystallization [8]. This means that the local order parameters of atoms with different equilibrium structures could be identical, especially in higher-temperature systems, in which the distributions of local order parameters become flatter and the

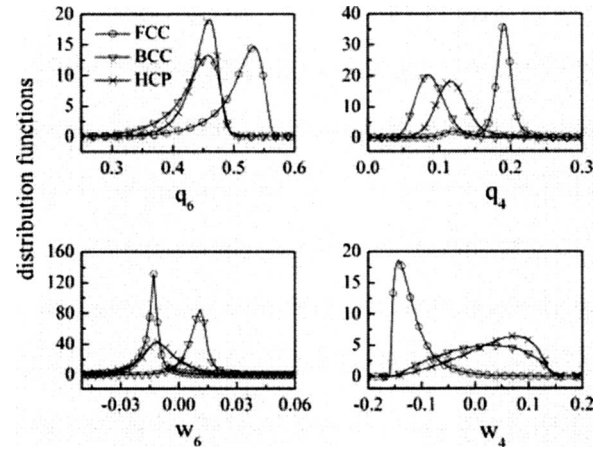


FIG. 1. Distributions of local order parameters  $q_6(i)$ ,  $q_4(i)$ ,  $w_6(i)$ , and  $w_4(i)$  in equilibrium fcc, hcp, and perturbed bcc lattices. All the results are based on averages over 20 independent configurations.

peak positions of the distributions depart from the corresponding ones in perfect structures. In fact, we have used the method of Volkov *et al.* to identify the perturbed bcc lattice; 82.22% and 17.65% of bcc atoms have been mistaken for hcp and fcc structures, respectively, while the same lattice can be recognized as bcc structure by the pair analysis method and Voronoi analysis method. Although one can attribute this to the artificial preparing method of bcc structure, that failure at least suggests a possible risk when this version of local order parameter method is applied, especially in supercooled liquids or solids at relatively higher temperatures.

### C. Pair analysis technique

In the pair analysis technique, a threshold value  $r_c$  is introduced to define neighbors as those distances  $r \leq r_c$ , and each pair of atoms is characterized by four indices [3,19]. The first index is assigned as 1 if the composing atoms of the pair are neighbors and 2 otherwise. The second index records the number of commonly neighboring atoms shared by the pair, and the third one represents the number of nearest-neighbor bonds between those commonly neighboring atoms. The fourth index is used to distinguish different topologies of atomic packings with the same first three indices. Different kinds of structures have their typical indices. For example, if we limit our discussion to the pairs bonded by neighboring atoms, only 1421 pairs are presented in the fcc crystal, while 1421 and 1422 pairs are contained in the hcp lattice. 1441 and 1661 are typical pairs of bcc lattices, and 1551 is considered as a direct measurement of the ico environments [3,20].

Generally, the pair indices vary with the threshold value  $r_c$ . Take the perfect bcc lattice as an example; if we only consider the first nearest neighbors, all the indices will be 1001. However, if both the first and second nearest neighbors are taken into account, the indices will be 1441 or 1661. Figure 2 shows the fraction of 1421 pairs as a function of  $r_c$  in equilibrium fcc crystals at different temperatures. The pair indices are more sensitive to  $r_c$  at higher temperatures, and

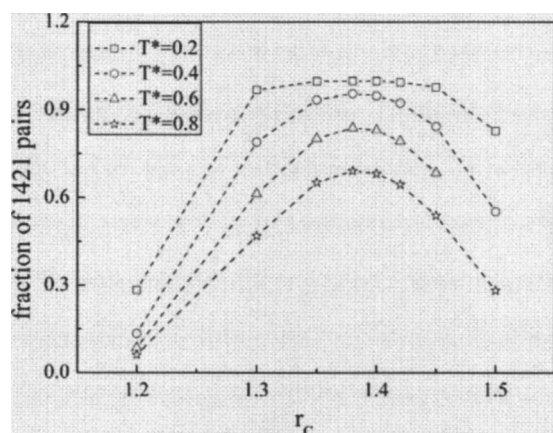


FIG. 2. Fractions of 1421 pairs in fcc lattices at different temperatures  $T^*$ , as a function of the threshold value  $r_c$ . The position of the first minimum in the RDF is 1.38 in each case.  $T^*$  and  $r_c$  are in reduced LJ units.

unreasonable results would be gathered if the threshold value  $r_c$  was not chosen properly. In fact, 1421 is easily mistaken for 1311, 1411, 1431, 1441, or even 1541. The optimal value of  $r_c$  is found to be at the position of the first minimum in the RDF for fcc and hcp lattices, and the second minimum in the RDF for bcc lattices.

Once we set  $r_c$  following the above principle (i.e., 1.38 for fcc or hcp lattices and 1.54 for bcc lattices in reduced units in our simulation), 83.80% of pairs are recognized as 1421 in fcc lattices at the temperature  $T^*=0.6$ . Percentages of the 1421 and 1422 pairs in hcp crystals at the same temperature are 42.07% and 42.29%, respectively, and 37.80% and 49.14% of pairs are identified as 1441 and 1661 in bcc lattices. Although the majority of the pairs are typical ones of the corresponding lattice, errors are larger than 10% in each case. In fact, because of the vibration of atoms in lattices, it is not very reasonable to take a single threshold value  $r_c$  to define neighboring atoms. The dependence of the pair indices on  $r_c$  will become more severe in supercooled liquids. It comes from the variety of pair indices and the heterogeneity of local structure [13–17,19]. Moreover, both the local structure and the position of the vale in the RDF shift during solidification. From these senses, the pair analysis technique only serves as an approximate structure analysis method for supercooled liquids in our opinion.

#### D. Voronoi analysis approach

The Voronoi polyhedron associated with a particle is defined as an assembly of points which are closer to that particle than any of the other particles in the system [22]. There are various ways to construct Voronoi polyhedra for a given configuration. The commonly used approaches in condensed matter physics and material science are attributed to Finney [28], Brostow *et al.* [29] and Tanemura *et al.* [30]. We choose here the algorithm proposed by Tanemura *et al.*, which seems to be more efficient than the former [30]. Delaunay tetrahedra, whose vertices are sets of four atoms contiguous with each other, are built at the first step in this

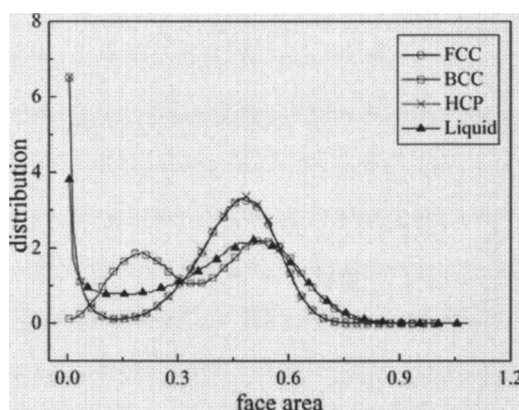


FIG. 3. Face area distributions of the Voronoi polyhedra for atoms in fcc, bcc, hcp, and liquid environments at the temperature  $T^*=0.6$ . Results are based on averages over ten independent configurations. The face areas are in reduced LJ units.

algorithm. The centers of the spheres circumscribing these Delaunay tetrahedra form the dual Voronoi vertices [30].

After the construction of Voronoi polyhedra, the face areas and edge lengths of Voronoi polyhedra are calculated. Figures 3 and 4 present the statistical distributions of the face areas and edge lengths for atoms in fcc, bcc, hcp, and liquid environments. The double peaks in the face area distribution for atoms in bcc lattices are due to four-sided faces and six-sided faces, respectively.

For fcc and hcp lattices, the distributions of the face areas and edge lengths are bimodal but separated by nonzero minima. The first peak originates from the distorted faces or edges due to thermal fluctuations and computational rounding errors, and the second peak results from the real faces or edges. The nonzero minima between them mean that the distorted faces and edges are too large to be distinguished from the real ones. Therefore, it is not reasonable enough to take a single threshold value to define these distorted faces or edges [24]. Particularly, we find that many distorted edges are not usually smaller than the edges associated with four-sided

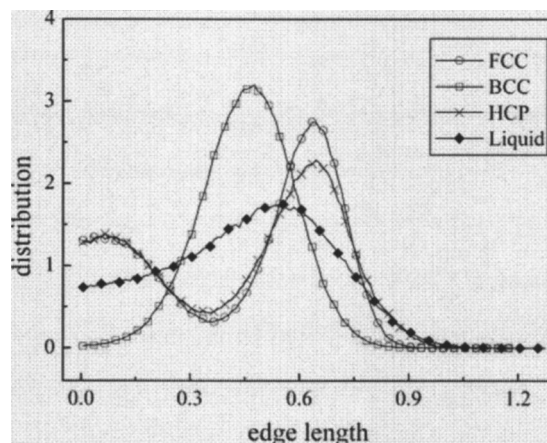


FIG. 4. Edge length distributions of the Voronoi polyhedra for atoms in fcc, bcc, hcp, and liquid environments at the temperature  $T^*=0.6$ . Results are based on averages over ten independent configurations. The edge lengths are in reduced LJ units.



TABLE I. Structure components and average number of survived faces (ANF) after different Voronoi face and edge elimination processes for different kinds of configurations. In the original method 1 (OM1), all the faces smaller than 0.1 and edges shorter than 0.15 are cut. Then an iteration process is used to eliminate small edges coupling with an upper edge length limit 0.4. In the original method 2 (OM2), the same procedure is applied but the parameters are 0.01, 0.05, and 0.4, respectively. All the results are based on averages over ten independent configurations.

Configurations	Methods	Structure components					ANF
		fcc	bcc	hcp	ico	Others	
fcc	This work	91.363%	0.250%	0.034%	0.025%	8.328%	11.994
	OM1	83.694%	0	0	0	16.306%	11.906
	OM2	59.850%	0.250%	0	0.025%	39.875%	12.282
bcc	This work	0	95.274%	0.134%	0	4.592%	13.914
	OM1	0.022%	45.373%	0.074%	0	54.534%	11.673
	OM2	0	95.293%	0	0	4.707%	13.793
hcp	This work	0	0.480%	90.998%	0.034%	8.488%	11.995
	OM1	0	0	75.920%	0	24.08%	11.897
	OM2	0	0.480%	55.281%	0.034%	44.205%	12.242
Liquid	This work	0	0	0	2.428%	97.572%	11.969
	OM1	0.081%	0	0.184%	1.091%	98.644%	10.146
	OM2	0.053%	0.063%	0.119%	1.847%	97.918%	11.113

faces. Note that the edges associated with four-sided faces are indispensable to the Voronoi polyhedron in fcc or hcp lattices.

Therefore, we introduce four threshold parameters  $a$ ,  $b$ ,  $x$ , and  $y$  to modify the distorted face and edge elimination procedure.  $a$  and  $b$  define the scales of “sightless” faces and edges generating from computational rounding errors.  $x$  specifies the maximum area of distorted faces, and  $y$  defines the maximum length of distorted edges from thermal vibrations and computational rounding errors. The procedure is executed as follows. First, choose a Voronoi polyhedron and eliminate all the faces smaller than  $a$  and all the edges shorter than  $b$ . If the Voronoi polyhedron belongs to the predefined structures—i.e., fcc, hcp, bcc, or ico environments—compute the next Voronoi polyhedron; otherwise, go to the second step. Second, find the smallest survived face. If the selected face is smaller than  $x$  and the total number of survived faces is more than 12, eliminate this face and repeat this step. If the total number of survived faces equals 12 and the Voronoi polyhedron does not belong to any predefined structures, switch to the third step; otherwise, compute the next Voronoi polyhedron. Third, find the surviving edges which are intersections between more than four-sided faces, and pick up the smallest one among them. If the selected edge is shorter than  $y$ , eliminate this edge. This step is iterated until a predefined structure is found or the selected edge is not shorter than  $y$ . Fourth, once the former three steps are executed over all atoms, a conventional cluster recognizing method [26] is applied to identify crystalline clusters of atoms with the same structures. The clusters that contain fewer than ten atoms are deleted and the atoms are assigned to liquid structure.

The first step in the above process is essential to reduce errors between different structures. For example, we have

found that a few Voronoi polyhedra with some tiny faces or edges are mistaken for bcc topologies in equilibrium fcc or hcp lattices. The parameters  $a$  and  $b$  are selected as 0.01 and 0.05, respectively, in our simulations, in order to ensure that the errors between different structures are less than 1%. The additional threshold parameters  $x$  and  $y$  are chosen to be slightly larger than the first minimum positions of the face area and edge length distributions for fcc and hcp environments. This turns out to be 0.2 and 0.4 in reduced units, respectively, in our simulation. With the modified procedure and parameters discussed above, more than 90% of atoms in crystalline solids are correctly identified, as shown in Table I. The distributions of face areas, edge lengths, and distances between nearest neighbors are monomodal and nearly smooth for supercooled liquid at the temperature  $T^* = 0.6$ , as shown in Figs. 5–7.

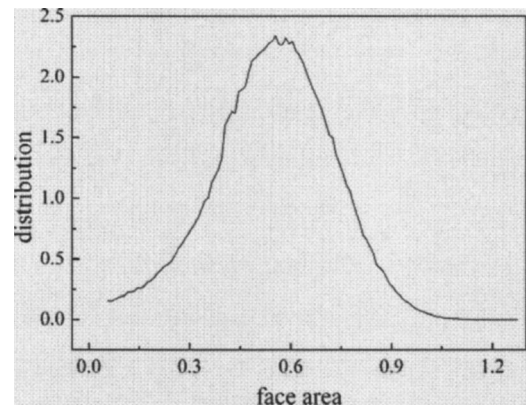


FIG. 5. Distributions of the survived face areas by the modified Voronoi face and edge elimination procedure. Results are based on averages over five independent configurations. The face areas are in reduced LJ units.

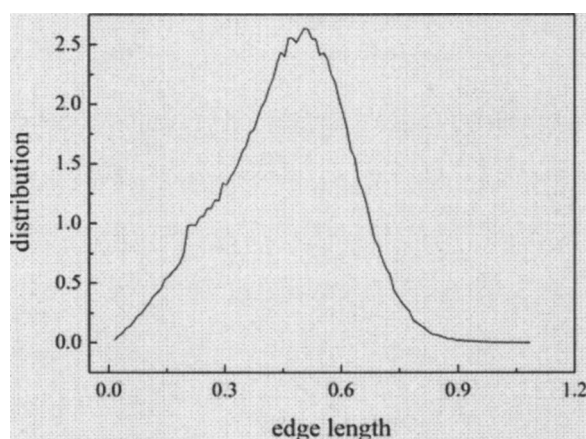


FIG. 6. Distributions of the survived edge lengths by the modified Voronoi face and edge elimination procedure. Results are based on averages over five independent configurations. The edge lengths are in reduced LJ units.

Table I also shows the comparison between the results of the modified process and those by the original method of Brostow *et al.* [24]. It is obvious that our process performs better in fcc and hcp lattices and well enough in bcc lattices. For supercooled liquid, the average numbers of survived faces are about 12 and 11 or even 10 in the results of our modified approach and the original method, respectively. The surviving Voronoi faces function as perpendicular bisectors between neighboring atoms. If we define two atoms as neighbors when their distance is less than the position of the first minimum in the RDF, the average number of neighbors per atom will be between 12 and 13. From the comparison, we believe that the modified process is safer for protecting Voronoi faces than the original methods are. The improvement benefits from two aspects: one is the separation of face and edge cutting processes, making the edge elimination not affect the number of Voronoi faces, and the other is the protection of edges in four-sided faces; it is very important for fcc or hcp lattices.

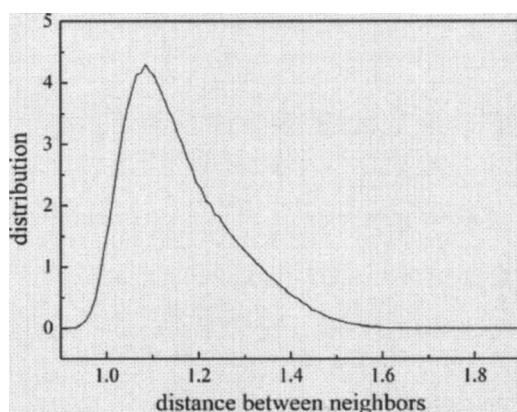


FIG. 7. Distributions of distances between nearest neighbors defined by Voronoi face with the modified Voronoi face and edge elimination procedure. Results are based on averages over five independent configurations. The distances are in reduced LJ units.

TABLE II. Fractions of pair indices in supercooled liquids at a temperature  $T^*=0.6$ . Nearest neighbors are defined as those distances  $r \leq r_c=1.50$ . All the results are based on averages over ten independent configurations.

Pairs	Fractions	Pairs	Fraction
1551	25.550%	1422	5.342%
1541	20.421%	1421	2.873%
1431	18.416%	1321	2.423%
1661	9.086%	1311	2.318%
1441	6.737%	Others	6.834%

### III. APPLICATIONS

The pair analysis technique and the Voronoi analysis method discussed above are employed to analyze the structure of supercooled liquid and its evolution during solidification. The systems are prepared using the same way as mentioned above. The temperatures are set as  $T^*=0.6$  and  $T^*=0.5$ , respectively. We find that the supercooled liquid at the temperature  $T^*=0.6$  stays in metastable state in 200 000 time steps, while solidification occurs in supercooled liquid at the temperature  $T^*=0.5$ .

Table II shows the diversity of pair indices in supercooled liquids at  $T^*=0.6$  by the pair analysis approach. The threshold value  $r_c$  is at the first minimum in the RDF as ordinarily taken [3,13–17,19–21]—i.e., 1.50 in reduced units. Although there is abundance of 1551, 1541, and 1431 pairs, atoms in liquid environments are usually bonded by a variety of pairs. This explains the reason why the fraction of atoms with ico environments is only 2.428% (shown in Table I), while the percentage of 1551 pairs is as great as 25.55%.

For supercooled liquid at the temperature  $T^*=0.5$ , the structure components and the fractions of pair indices vary with time. The time evolutions of structure components, which are gathered by the Voronoi analysis method combined with the modified face and edge elimination process, are shown in Fig. 8. At the initial stage, the fraction of atoms with ico environments decreases rapidly, while the percent-

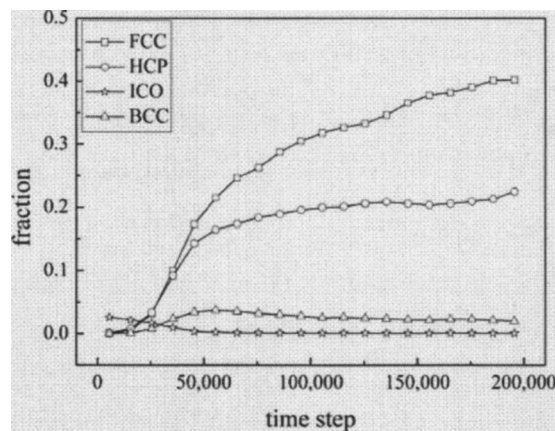


FIG. 8. Evolution of structure components in supercooled LJ liquids at the temperature  $T^*=0.5$  by Voronoi analysis method. Results are based on averages over ten independent configurations.

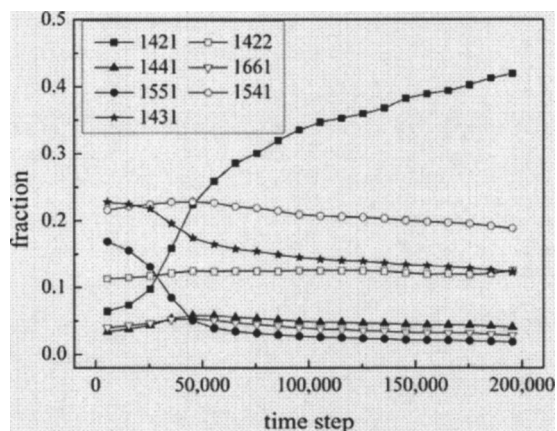


FIG. 9. Evolution of pair indices in supercooled LJ liquids at  $T^* = 0.5$  by pair analysis method. Results are based on averages over ten independent configurations.  $r_c$  is 1.45 in reduced LJ units.

ages of fcc and hcp atoms increase. This suggests that the stability of metastable liquids is correlated with the existence of ico structures [1,3,4,12,18]. The fraction of bcc atoms increases at the beginning and then decreases.

Comparing our simulation results with those of Swope and Andersen [4], we notice that the percentage of hcp atoms is somehow larger and the fraction of bcc atoms decrease slower in our simulation. The percentage of hcp atoms acts alike that in the work of O' Malley and Snook [10] in hard-sphere systems. We believe that the discrepancies come from the differences of the system conditions under consideration. The microstructure evolution in supercooled liquids should be considered associated with the thermodynamic conditions and the initial structure of the system [4,6,12].

Figures 9 and 10 present the evolution of pair indices. In Fig. 9, we take the definition of nearest neighbors as those whose distances are shorter than  $r_c = 1.45$ . This threshold value equals the average of the first minimum positions in radial distribution functions before and after solidification. The value of  $r_c$  is updated during the evolution of the system,

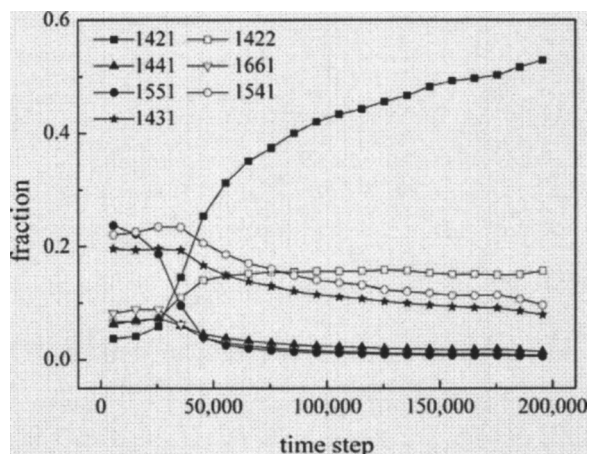


FIG. 10. Evolution of pair indices in supercooled LJ liquids at  $T^* = 0.5$  by pair analysis method. Results are based on averages over ten independent configurations. The value of  $r_c$  is updated immediately during the system evolution.

as indicated in Fig. 10. In both figures, the decrease of the 1551 pairs is accompanied by an increase of the 1421 pairs. For the fraction of 1422 pairs, Fig. 9 shows a much slower increase than Fig. 10. In this sense, Fig. 10 is more consistent with Fig. 8. The 1441, 1661, 1431, and 1541 pairs also show similar while different in quantity trends in both figures. The differences between Figs. 9 and 10 provide evidence that the pair indices are sensitive to the neighborhood definition in supercooled liquids.

When compared with the analysis of Swope and Andersen [4], the Voronoi analysis method combined with our modified face and edge elimination process is more stable and reliable, as shown in Fig. 8. Moreover, the results from the pair analysis technique, where the threshold value  $r_c$  is taken to be at the first minimum position of the RDF, and from the Voronoi analysis method, combined with our modified face and edge cutting processes, are qualitatively consistent with each other.

#### IV. CONCLUSIONS

We have examined the three most widely used microstructure analysis methods in equilibrium fcc, hcp, and randomly perturbed bcc crystalline solids and supercooled liquids.

The distributions of local order parameters from different crystalline structures intersect with each other, and the local order parameter approach due to Volkov *et al.* [11] fails in a randomly perturbed bcc lattice.

The pair analysis technique behaves as an approximate approach depending on how the neighborhood is defined. The pair indices become more sensitive to  $r_c$  at higher temperatures. The optimal value of  $r_c$  is at the position of the first minimum in the RDF for fcc and hcp lattices, and the second minimum in the RDF for bcc lattices.

The face area and edge length distributions are bimodal and separated by nonzero minima in equilibrium fcc and hcp lattices. The extra edges resulting from thermal vibrations are comparable to real edges at the higher temperatures relevant to supercooled liquids. In order to protect real edges, especially those in four-sided faces of fcc and hcp lattices, we modify the Voronoi face and edge elimination processes. Compared with the original methods, our modified approach performs better in fcc and hcp lattices, safer in supercooled liquids, and well enough in bcc lattices. The parameters in the modified procedure could be a little bit different, in order to get more precise results in different cases. The separation of the face and edge cutting procedures, the iteration process for cutting edges [24], and the protection of edges in four-sided faces are important in the Voronoi analysis method, especially for supercooled liquids.

Qualitatively consistent results are attained when the pair analysis technique and the Voronoi analysis method are properly applied to catch the information of microstructure and its evolution in supercooled liquids.

#### ACKNOWLEDGMENT

Financial support from the National Natural Science Foundation of China (Grant No. 50395101) is gratefully acknowledged.



- [1] P. G. Debenedetti, *Metastable Liquids: Concepts and Principles* (Princeton University Press, Princeton, 1996).
- [2] J. R. Errington, P. G. Debenedetti, and S. Torquato, *Phys. Rev. Lett.* **89**, 215503 (2002).
- [3] H. Jonsson and H. C. Andersen, *Phys. Rev. Lett.* **60**, 2295 (1988).
- [4] W. C. Swope and H. C. Andersen, *Phys. Rev. B* **41**, 7042 (1990).
- [5] P. R. ten Wolde, M. J. Ruiz-Montero, and D. Frenkel, *J. Chem. Phys.* **104**, 9932 (1996).
- [6] P. R. ten Wolde, M. J. Ruiz-Montero, and D. Frenkel, *Phys. Rev. Lett.* **75**, 2714 (1995).
- [7] S. Auer and D. Frenkel, *Nature (London)* **409**, 1020 (2001).
- [8] U. Gasser, E. R. Weeks, A. Schofield, P. N. Pusey, and D. A. Weitz, *Science* **292**, 258 (2001).
- [9] V. J. Anderson and H. N. W. Lekkerkerker, *Nature (London)* **416**, 811 (2002).
- [10] B. O'Malley and I. Snook, *Phys. Rev. Lett.* **90**, 085702 (2003).
- [11] I. Volkov, M. Cieplak, J. Koplik, and J. R. Banavar, *Phys. Rev. E* **66**, 061401 (2002).
- [12] K. F. Kelton, G. W. Lee, A. K. Gangopadhyay, R. W. Hyers, T. J. Rathz, J. R. Rogers, M. B. Robinson, and D. S. Robinson, *Phys. Rev. Lett.* **90**, 195504 (2003).
- [13] N. Jakse and A. Pasturel, *Phys. Rev. Lett.* **91**, 195501 (2003).
- [14] N. Jakse, O. Le Bacq, and A. Pasturel, *Phys. Rev. B* **70**, 174203 (2004).
- [15] N. Jakse, O. Le Bacq, and A. Pasturel, *Phys. Rev. Lett.* **93**, 207801 (2004).
- [16] N. Jakse and A. Pasturel, *J. Chem. Phys.* **120**, 6124 (2004).
- [17] L. Hui and F. Pederiva, *Phys. Rev. B* **68**, 054210 (2003).
- [18] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, *Phys. Rev. B* **28**, 784 (1983).
- [19] J. D. Honeycutt and H. C. Andersen, *J. Phys. Chem.* **91**, 4950 (1987).
- [20] D. W. Qi and S. Wang, *Phys. Rev. B* **44**, R884 (1991).
- [21] Li Hui, Wang Guanghou, Bian Xiufang, and D. Feng, *Phys. Rev. B* **65**, 035411 (2001).
- [22] J. L. Finney, *Proc. R. Soc. London, Ser. A* **319**, 479 (1970).
- [23] C. S. Hsu and A. Rahman, *J. Chem. Phys.* **71**, 4974 (1979).
- [24] W. Brostow, M. Chybicki, R. Laskowski, and J. Rybicki, *Phys. Rev. B* **57**, 13448 (1998).
- [25] W. G. Hoover, A. J. C. Ladd, and B. Moran, *Phys. Rev. Lett.* **48**, 1818 (1982).
- [26] D. C. Rapaport, *The Art of Molecular Dynamics Simulation* (Cambridge University Press, Cambridge, England, 1995).
- [27] D. Brown and J. H. R. Clarke, *Mol. Phys.* **51**, 1243 (1984).
- [28] J. L. Finney, *J. Comput. Phys.* **32**, 137 (1979).
- [29] W. Brostow, J.-P. Dussault, and B. L. Fox, *J. Comput. Phys.* **29**, 81 (1978).
- [30] M. Tanemura, T. Ogawa, and N. Ogita, *J. Comput. Phys.* **51**, 191 (1983).