Polytetrahedral Nature of the Dense Disordered Packings of Hard Spheres

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We study the structure of numerically simulated hard sphere packings at different densities by investigating local tetrahedral configurations of the spheres. Clusters of tetrahedra adjacent by faces present relatively dense aggregates of spheres atypical for crystals. The number of spheres participating in such polytetrahedral configurations increases with densification of the packing, and at the Bernal's limiting density (the packing fraction around 0.64) all spheres of the packing become involved in such tetrahedra. Thus the polytetrahedral packing cannot provide further increase in the density, and alternative structural change (formation of crystalline nuclei) begins henceforth.

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The model of hard spheres is widely used in structural studies of liquids, glasses, colloids, and granular materials. It successfully reproduces the main structural properties of the condensed phase, such as crystallization of liquids [1,2] and amorphous solid phase transition [3,4]. The wide applicability of this simple model reflects the fact that the structure of dense matter is determined first of all by impenetrability of atoms, and ultimately comes from geometric properties of the packings of nonoverlapping spheres in three-dimensional space [5].

In this work we study a characteristic feature of dense disordered packings of spherical particles—the presence of *tetrahedral* configurations, which in turn join together forming *polytetrahedral* aggregates of spheres. The important properties of these aggregates are, on the one hand, rather high local density, and, on the other hand, their incompatibility with crystalline structures. It is commonly believed that this promotes stability of the disordered phase, and prevents crystallization of liquids. This idea was first suggested by Frank in 1952 to explain supercooling of liquid metals [6]. He showed that the icosahedral configuration of atoms (a compact cluster of 20 tetrahedra) has a lower potential energy than a crystalline fragment built from these atoms, but the icosahedron has fivefold symmetry axes forbidden for translational symmetry. Since then many works have appeared in which the authors were deliberately searching for *icosahedral* local order in liquids, using both physical experiment [7–9] and computer simulation [3,10–13]. However, tetrahedra can join not only into icosahedra, but also in other, quite different aggregates [13–17]. The analysis of computer models has long demonstrated that tetrahedra prefer to form branching linear clusters with five-membered rings [15,16], and icosahedra *per se* are rarely found in monoatomic disordered systems, as pointed out, e.g., in the works [2,17,18] that specifically investigated this question. It is thus more correct to refer not to icosahedral, but rather to *polytetrahedral* structure of simple liquids [5,13,19]. Note that conclusions inferred from analysis of pair interatomic distances (as provided from diffraction experiments) can only say about the presence of face-adjacent tetrahedra because such clusters contain all pair distances that are present in icosahedron.

First studies of disordered hard sphere packings were started by Bernal on mechanical packings of steel balls [5]. He noted that a disordered packing has a limiting (critical) density that is a packing with higher density contain crystalline regions inevitably. Physical experiments give an estimate of 0.637-0.64 for this density [5,20,21], computer simulations provide the very close values (0.637–0.645) [3,4,22–26]. What is important, this density is substantially lower than the maximum packing fraction attainable in the densest crystalline structures, $\pi/\sqrt{18} \approx 0.74$. The origin of the critical density for disordered packing and its precise value are not known today despite the substantial effort that has been put into this study. It is unclear what geometrical principle is at work in disordered packing and why it is limited at a density of about 0.64. This problem still remains a challenge for both physicists and mathematicians [5,27]. It looks like "a disordered analog" of the Kepler conjecture for the densest crystalline packing of spheres [28,29], which had been proved only recently [29,30]. We suggest that the answers to these questions can be sought in the study of the structure of polytetrahedral aggregates.

In this Letter we show that aggregates of face-adjacent tetrahedra are the essential feature of the dense disordered packings. Such a principle of structural organization seems to be preferable from the statistical viewpoint, as in this case a broad range of dense local configurations can be realized. However, it does have its limit, as higher densities can only be reached with crystalline placement of spheres.

We study a large set of hard sphere packings (about 300) with packing density from 0.53–0.71. Each packing contains 10 000 identical hard spheres in a model box with periodic boundary conditions. More then 200 packings were obtained using a modified Jodrey-Torey algorithm that employs "repulsion" of overlapping spheres with gradual reduction of their radii [23,31]. This algorithm can easily produce not only disordered packings with densities up to the limiting value, but also more dense systems containing crystalline structures [17,31]. To test the independence of structure on the algorithms used for packing generation we also computed a series of 70 packings in the range of densities from 0.54–0.67 using the Lubachevsky-Stillinger algorithm [25]. This algorithm employs a different procedure for raising the density: a molecular dynamics of nonoverlapping spheres with gradual increase of their radii.

All our packings can be considered to be "maximally disordered at a given density." When generating them we each time start from a random initial configuration of spheres and using the quickest way "lead" it into the desired density. It is easy to make by an appropriate choice of the parameters of the algorithms [32]. As a result, for densities below the limiting value, disordered packings are always produced. At higher densities crystallization naturally begins, and nuclei with face centered cubic (fcc) and hexagonal close packing (hcp) structures of different morphologies arise in the packings.

As our additional analysis shows, independent packings having the same densities demonstrate similar structures; i.e., the pair correlation functions and standard statistical characteristics of Voronoi polyhedra and Delaunay simplexes [31] for such packings are practically identical. The representativeness of our models is further illustrated by a fairly good coincidence of points for each given density on the figures below, where each point represents an independent packing.

Before starting the investigation of polytetrahedral aggregates it is necessary to determine basic configurations of four spheres which should be considered. There is a general approach in geometry that allows unambiguous selection of the closest quadruples for an arbitrary system of discrete points (sphere centers). This is done using the Voronoi-Delaunay partitioning, well known both in physics and mathematics [33]. A tetrahedron of a general shape with vertices in these four spheres is called *Delaunay simplex*. The Delaunay simplexes are a very convenient tool for various structural studies [34]. They are the simplest elements of the three-dimensional structure. Any cluster of Delaunay simplexes represents a fragment of a packing (an aggregate of the spheres). Thus, to study the structure of a packing first Delaunay simplexes are calculated, then their shape is analyzed to pick simplexes of tetrahedral shape, and finally the clusters of such simplexes are studied.

There are several possible criteria to evaluate the shape of a simplex quantitatively [30,34,35]. In this Letter we use a simple but efficient approach based on the maximal simplex edge length $e_{\max}$ [30]. It is especially suitable for identical hard spheres, where the diameter of the sphere sets the minimal possible length of the simplex edge taken as 1. In this Letter we will use this approach calculating the difference of the maximal edge lengths from unit

$$\delta = e_{\max} - 1.$$

Small values of δ unambiguously indicate that the shape of the simplex is close to regular tetrahedron with unit edges.

A substantial point in identification of the tetrahedra is determination of a boundary for the used measure. In the proof of the Kepler conjecture [29,30] Hales chose 2.51 of the radius of the sphere as a boundary edge length for tetrahedral simplexes. In our notation it corresponds to $\delta = 0.255$. Hales found this boundary in his research by trial, and named the class of simplexes selected by $\delta < 0.255$ as "quasiregular tetrahedra" (or simply tetrahedra). In this work we use this condition to select tetrahedra. However, to be more sure in physical results obtained we also employ lower boundary values (0.20 and 0.15) selecting simplexes with the better tetrahedral shape.

For each packing from our set of models we calculated Delaunay simplexes and picked those of them that had tetrahedral shape according to our criteria. Figure 1 shows the portion of space occupied by the tetrahedral Delaunay simplexes in packings via the packing density. Different curves correspond to different shape regularity of the selected tetrahedra.

The fraction of tetrahedra rapidly grows with density, and for the curve with $\delta < 0.255$ they occupy about 30% of volume when approaching the density around of 0.64. This confirms the old qualitative conclusions that dense disordered packings of spherical atoms contain many tetrahedral configurations [5,15]. Tetrahedra with better shape are also present in noticeable amounts, and their fractions grow with acceleration up to the same limiting density. After that point their curves grow linearly according to raise and improving of crystalline order. Recall the value

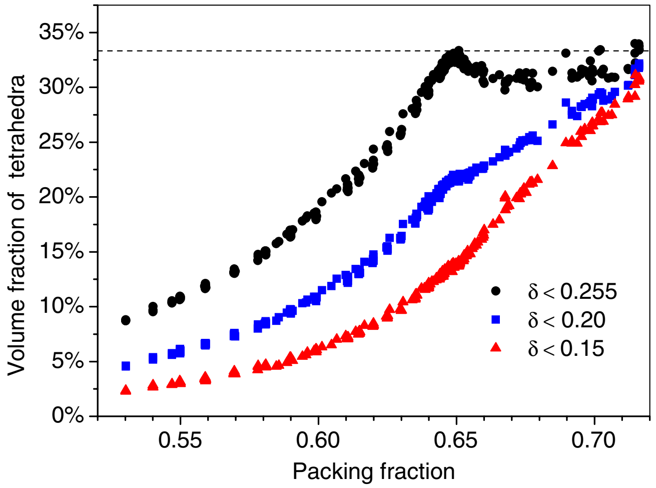

FIG. 1 (color online). Volume fraction of a packing occupied by tetrahedral configurations as a function of packing density. Different curves correspond to different criteria for selection of the tetrahedra: $\delta = 0.255$, 0.20, and 0.15, from top to bottom. Every symbol corresponds to one of the packings. Dashed horizontal line corresponds to value 1/3.

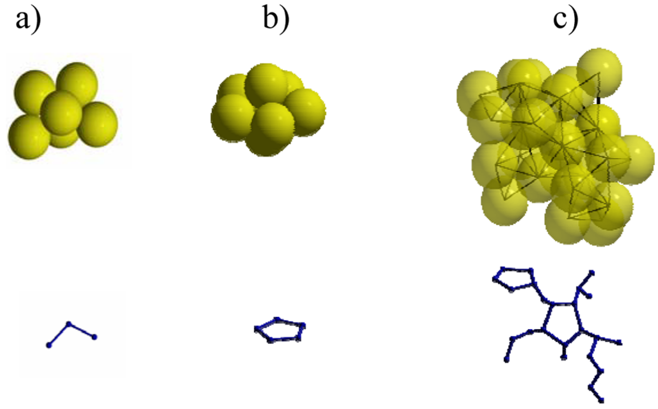

FIG. 2 (color online). Examples of polytetrahedral aggregates (clusters of face-adjacent tetrahedra). (a) three tetrahedra, (b) a ring of five tetrahedra, (c) a typical polytetrahedral cluster in dense disordered packing. The lower row shows motifs of the clusters: the points mark the centers of the tetrahedra, and the lines indicate that they are adjacent through a common face.

1/3 corresponds to the fraction of volume occupied by tetrahedra in the densest crystalline structures fcc and hcp.

In the class of polytetrahedral aggregates (polytetrahedra) we put clusters built from three or more face-adjacent tetrahedra, Fig. 2. Isolated tetrahedra and pairs of tetrahedra (bipyramids) are omitted as they are found in the fcc and hcp crystalline structures. In the general case polytetrahedra have the form of branching chains and five-member rings combining in various "animals" [15–17].

Figure 3 shows the fraction of volume contained in polytetrahedra as a function of packing density. The behavior of these curves is quite different from the curves in Fig. 1. For disordered packings a similarly rapid growth with density is observed. Upon approaching the limiting density they account also for about 30% of volume (for the criterion $\delta < 0.255$) as it was for the total amount of tetrahedra in Fig. 1. This means nearly all tetrahedra in the packing have coalesced into polytetrahedral aggregates at this density. However, after the limiting density the number of polytetrahedra sharply decreases. This is an obvious consequence of forming fcc and hcp crystalline structures, in which tetrahedra prefer to have neighbors through their edges or form bipyramids. The same behavior is demonstrated by tetrahedra of the better shape, $\delta < 0.20$ and $\delta < 0.15$. At the limiting density, a majority of them are also coalesced in polytetrahedra.

A specific behavior of the curves in Fig. 3 (quick rise and sharp fall) demonstrates a "critical character" of the structural transformation at the limiting density. The position of the peaks (we estimate it as 0.646) does not depend visibly on the quality of selected tetrahedra. It means disintegration of the polytetrahedra begins simultaneously regardless of criterion used for tetrahedral shape.

Figure 3 clearly demonstrates the polytetrahedral nature of the disordered hard sphere packings. The increase of the density before the Bernal's limit occurs via growth of the number of tetrahedral configurations and their coalescence into polytetrahedral aggregates. The question then arises why this principle stops working for high density? What resource of packing becomes exhausted upon approaching the limiting density? Figure 4 demonstrates that the parameter reaching its limit is the number of spheres involved in formation of tetrahedra. For each packing we counted the spheres that are a vertex of at least one tetrahedron. Each sphere of the packing is a common vertex for several

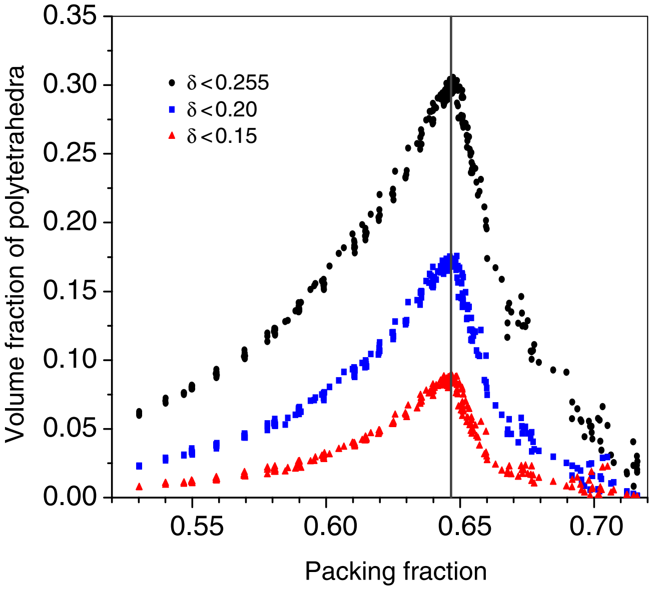

FIG. 3 (color online). Volume fraction occupied by polytetrahedral aggregates (Fig. 2) as a function of packing density. Different curves correspond to different quality of the selected tetrahedra. Vertical lines correspond to a packing fraction of 0.646.

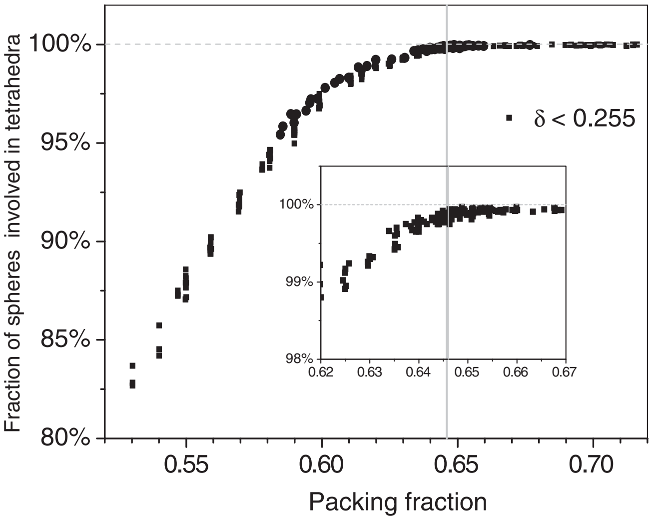

FIG. 4. Fraction of hard spheres in the packing involved in tetrahedra as a function of packing density. The inset shows a blowup of the region in the vicinity of the limiting density.

Delaunay simplexes [33]. If at least one of them is a tetrahedron we count this sphere. As can be seen, the fraction of these spheres grows with increasing density and reaches 100% just at the limiting density. The inset in Fig. 4 shows a blowup of the region in the vicinity of limiting density. Upon reaching this density only a very small fraction of spheres avoid involvement in tetrahedra. These can be considered as rare events and omitted, as packings with crystalline structures have about the same number of such ‘‘not accounted for’’ spheres.

Thus, an increase in the density of a disordered packing occurs via an increase in the number of tetrahedral configurations that coalesce into irregular polytetrahedra. This process is sustained by involving more and more spheres into tetrahedra. However, after all spheres of the system have been involved, a further densification would require another mechanism to increase the density of the packing.

The performed analysis of computer models of dense packings of identical hard spheres in a wide range of densities demonstrates that a characteristic feature of disordered packings is their polytetrahedral structure; i.e., the packings contain an appreciable fraction of tetrahedral configurations that prefer to coalesce via their faces to form locally dense aggregates of various morphology incompatible with translational symmetry. Such tetrahedra are not perfect, i.e., not all spheres are in contact, and the gaps between the neighboring spheres may be as large as 25% of the diameter. These tetrahedra coincide with the class of quasiregular tetrahedra introduced by Hales in his proof of the Kepler conjecture. The fraction of polytetrahedral aggregates grows with the density of the disordered packing. Upon reaching the limiting density all spheres of the packing become involved in construction of the tetrahedra. Any further increase in density within this ‘‘polytetrahedral’’ principle of packing at this point becomes impossible.

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