Structural Properties of Dense Hard Sphere Packings

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ABSTRACT: We numerically study structural properties of mechanically stable packings of hard spheres (HS), in a wide range of packing fractions 0.53 \( \leq \phi \leq 0.72 \). Detailed structural information is obtained from the analysis of orientational order parameters, which clearly reveals a disorder–order phase transition at the random close packing (RCP) density, \( \phi_c \approx 0.64 \). Above \( \phi_c \), the crystalline nuclei form 3D-like clusters, which upon further desiccation transform into alternating planar-like layers. We also find that particles with icosahedral symmetry survive only in a narrow density range in the vicinity of the RCP transition.

INTRODUCTION

As a fundamental model in condensed matter physics and material science, packings of hard spheres (HS) reproduce many essential structural properties of glassy and granular media.\(^1\)–\(^3\) Structural changes of the HS system have been observed when a packing is densified above the density of random close packing (RCP)\(^4\), \( \phi_c \approx 0.64 \) (see, e.g., refs 5 and 6). A new order parameter, which is based on the cumulative distribution of the rotational invariant \( w_\phi \) was proposed in ref 5 to identify these structural changes. Random arrangement is transferred to partial crystallization across RCP, and two lattice types, the face centered cubic (fcc) and the hexagonal close-packed (hcp), are observed in the crystalline clusters. However, more detailed information has not been obtained due to insufficient system size. In this study, we aim to explore more detailed structural changes of the transition at RCP in comparison with previous studies,\(^5,6\) based on larger scale simulations.

We numerically generate a large set of HS packings composed of \( N = 64 \times 10^3 \) monodispersed spheres located in the cubic box with periodic boundary conditions using the modified Lubachevsky–Stillinger (LS) algorithm.\(^7\)

RESULTS

To examine the structural properties of jammed spheres, we first study their spatial correlations. Figure 1 shows the radial distribution function \( g(r) \) of hard spheres for several different packing fractions in the range [0.60, 0.68]. The cumulative function \( Z(r) \equiv 4\pi r^2 g(r) dr \), which is the mean number of particles inside a sphere of radius \( r \), is also plotted in Figure 1. When \( \phi \leq \phi_c \), addition to the strong peaks at the contact distances \( r = 1, 2, \ldots \) (we set unit diameter), a weak secondary peak at \( r = (3)^{1/2} \) is visible. This peak corresponds to a contact angle \( \theta = 2\pi/3 \) but not necessarily a lattice structure.\(^8\) Above \( \phi_c \), additional peaks appear at \( (2)^{1/2}, (8/3)^{1/2}, \) and \( (11/3)^{1/2} \), which are typical distances in the fcc and hcp lattices. The observation indicates the onset of crystallization when the packings are densified above \( \phi_c \).

More detailed structural information can be obtained from the well-known bond order parameter method,\(^9\) which is widely used to study the structural properties of condensed matter.\(^9\)–\(^11\) hard spheres,\(^12\)–\(^19\) Lennard-Jones systems,\(^20\)–\(^24\) complex plasmas,\(^25\)–\(^34\) colloidal and patchy systems,\(^35\)–\(^37\) granular media,\(^38\) metallic glasses,\(^39\) repulsive shoulder systems,\(^40\) etc. Each particle

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$i$ is connected via vectors (bonds) with its $N_{nn}(i)$ nearest neighbors (NN), and the rotational invariants (RIs) of rank $l$ of second $q_l(i)$ and third $w_l(i)$ orders are calculated as

$$q_l(i) = \left( \frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_{lm}(i)|^2 \right)^{1/2}$$

$$w_l(i) = \sum_{m_1, m_2, m_3, m_4} \left[ \begin{array}{ccc} l & l & l \\ m_1 & m_2 & m_3 \\ m_4 & m_5 & m_6 \end{array} \right] q_{m_1}(i) q_{m_2}(i) q_{m_3}(i) q_{m_4}(i)$$

where $q_{lm}(i) = N_{nn}(i)^{-1} \sum_{j} Y_{lm}(r_{ij})$, $Y_{lm}$ are the spherical harmonics, and $r_{ij} = r_i - r_j$ are vectors connecting centers of particles $i$ and $j$. In eq 2, $\left[ \begin{array}{ccc} l & l & l \\ m_1 & m_2 & m_3 \end{array} \right]$ are the Wigner 3j-symbols, and the summations performed over all the indexes $m_1 = -l, ..., l$ satisfying the condition $m_1 + m_2 + m_3 = 0$. As shown in the pioneer paper, the bond order parameters $q_l$ and $w_l$ can be used as measures, to characterize the local orientational order and the phase state of considered systems. Because each lattice type has a unique set of bond order parameters, the method of RIs can also be used to identify lattice structures in mixed systems. The values of $q_l$ and $w_l$ for a few common lattice types (including the liquid-like HS state) are presented in Table 1. Some of the values were reported previously (see, e.g., refs 9 and 41–44). From eq 2, it is easy to see that $w_l \propto q_l^2$, and therefore, we expect $w_l$’s to be more sensitive measures compared to $q_l$’s.

In three dimensions (3D), the densest possible packings of identical hard spheres are the fcc and hcp lattices (with the densest packing fraction (pf) $\phi_{f hc} = \phi_{f c c} = (2\pi/6)^{1/3} \approx 0.74$). Dense HS systems may also include particles having the icosahedral (ico) type of symmetry. Icosahedral, fcc, and hcp spheres have 12 nearest neighbors (the spheres located in the first coordination shell).

To identify lattice-like particles, we calculate the bond order parameters $q_l$ and $w_l$ $(l = 4, 6)$ for each particle with a fixed number of the nearest neighbors $N_{nn} = 12$. A particle is called fcc-like (hcp-like, ico-like) if its coordinates in the four-dimensional space $(q_4, q_6, w_4, w_6)$ are sufficiently close to those of the perfect fcc (hcp, ico) lattice type. An amorphous (liquid-like) particle is identified if its order parameters are sufficiently small, for example, $q_6^{\text{am}} \approx N_{nn}^{-1/2} \approx 0.29 < q_6^{f c c/h c p/ i c o}$. Note that, by varying the NN number and rank $l$ of parameters $w_l$ and $q_l$, in principle, it is possible to find any lattice type. For instance, the first and second (next nearest neighbors) shells of body centered cubic (bcc) lattices correspond to $N_{nn} = 8$ and 14, respectively.

To quantify the local orientational order, it is convenient to use the probability distribution functions (PDFs) $P(q_l)$ and $P(w_l)$.

Table 1. Bond Order Parameters $q_l$ and $w_l$ $(l = 4, 6)$ for Several Typical Lattices and Liquid-Like HS Random Packings (rp) at $\phi = 0.55$, Calculated via the Fixed Number of Nearest Neighbors (NN)

<table>
<thead>
<tr>
<th>lattice type</th>
<th>$q_4$</th>
<th>$q_6$</th>
<th>$w_4$</th>
<th>$w_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hcp (12 NN)</td>
<td>0.097</td>
<td>0.485</td>
<td>0.134</td>
<td>−0.012</td>
</tr>
<tr>
<td>fcc (12 NN)</td>
<td>0.19</td>
<td>0.575</td>
<td>−0.159</td>
<td>−0.013</td>
</tr>
<tr>
<td>ico (12 NN)</td>
<td>$1.4 \times 10^{-3}$</td>
<td>0.663</td>
<td>−0.159</td>
<td>−0.169</td>
</tr>
<tr>
<td>bcc (8 NN)</td>
<td>0.5</td>
<td>0.628</td>
<td>−0.159</td>
<td>0.013</td>
</tr>
<tr>
<td>bcc (14 NN)</td>
<td>0.036</td>
<td>0.51</td>
<td>0.159</td>
<td>0.013</td>
</tr>
<tr>
<td>rp at $\phi = 0.55$ (12 NN)</td>
<td>$\approx 0.16$</td>
<td>$\approx 0.34$</td>
<td>$\approx −0.019$</td>
<td>$\approx −0.032$</td>
</tr>
</tbody>
</table>

Figure 2 shows how the PDFs vary at different $l$ $(l = 4, 6)$ and $\phi$ (covering both amorphous and solid-like states). Densification of the HS, as clearly seen in Figure 2, results in appearance of the crystalline fcc-like and hcp-like spheres in the vicinity of the RCP. Corresponding cumulative distributions $C_q$ and $C_w$ (shown by dashed lines of the same color) are also plotted in Figure 2. For instance, the cumulative function $C_q$ associated with the $P(q_l)$ is defined as

$$C_q(x) \equiv \int_{-\infty}^{x} P(q_l) \, dq_l$$
Evidently, $C_q(x)$ is the abundance of particles, having values of $q_i < x$ and $C_q(\infty) = 1$. Figure 3 shows two-dimensional PDFs—

![Figure 3](image)

Figure 3. Probability distributions on the order parameter plane of $q_i$—$q_6$ in the vicinity of the RCP at $\phi = 0.64$ (a) and $\phi = 0.65$ (b). Loci of the perfect fcc, hcp, and ico are also indicated on the plot. An fcc peak appears at $\phi = 0.65$. Note that the hcp lattice may have a large overlap with the liquid-like structure in this plot.

probability distributions on the plane $q_i$—$q_6$—in the vicinity of the RCP at $\phi \approx 0.64$ and $\phi \approx 0.65$. At $\phi \approx 0.64$, structurally HS is amorphous, while at $\phi \approx 0.65$ the formation of crystalline fcc-like spheres is clearly seen. The result suggests a disordered—ordered transition in the density range [0.64, 0.65], consistent with previous studies.6,16

The global order parameters, i.e., the cumulant $W_6^q$ (defined as $C_q(W_6^q) = 1/2$) and the mean value of $q_6$ (defined from the global averaging $\langle q_6 \rangle = (1/N) \sum_{i=1}^{N} q_6(i)$), are shown in Figure 4. No significant finite size effects are observed between $N = 10^4$ and $N = 64 \times 10^3$ systems. For the purpose of detecting crystallization onset, we find $W_6^q$ to be a more sensitive measure than $\langle q_6 \rangle$. This is because (1) liquid-like and lattice-like spheres have quite different values of $w_6$ and (2) $w_6$ is nearly the same for perfect fcc and hcp lattices (see Table 1). Because of this reason, the measure $W_6^q$ has been recently used to describe the melting and freezing phase transitions of Lennard-Jones23,24 and Yukawa systems.32–34 On the other side, the density dependence of $\langle q_6 \rangle$ also reveals fascinating properties. The relatively slow increase of $\langle q_6 \rangle$ at $\phi < \phi_c$ can be attributed to single hcp-like particles,5 while at $\phi > \phi_c$, the bond order parameter $\langle q_6 \rangle$ increases more rapidly due to the emergence of crystalline clusters. Further densification of the HS leads to strong fluctuations (“oscillations”) of the global parameter $\langle q_6 \rangle$ which start at $\phi \approx 0.68$ and suggest another transition.5 This oscillatory behavior is due to the fact that the hcp and fcc crystalline structures are characterized by quite different values of the bond order parameter $q_6$ (see Table 1), and at a given $\phi_c$ dense partially crystallized HS packings can be realized with quite different abundances of hcp-like and fcc-like spheres. Another important parameter characterizing the local structure is the abundance $N_w$ of spheres having icosahedral-type (5-fold) symmetry (see Figure 4, inset). Here, ico-like spheres are defined as spheres having $q_6 \geq 0.61$. The density dependence of $N_w$ shows that ico-like spheres can exist only in a narrow range of $\phi_c$, and its abundance maximizes at $\phi_c$.

The above analysis provides detailed information about the local and global orders. Next, we study the abundance of crystalline particles and their spatial arrangement. We use the standard friends-of-friends algorithm46 to find crystalline clusters. Figure 5 presents the spatial distribution and the shape of crystalline clusters composed of hcp- and fcc-like spheres, at several different $\phi$. When $\phi < 0.65$ (Figure 5a,b), the crystalline particles are mostly isolated; increase of packing fraction $\phi$ leads to an appearance of several 3D (containing tens of spheres, both hcp- and fcc-type) clusters (Figure 5c,d at $\phi \approx 0.66$). Upon further densification, these 3D clusters transform into 2D layers spanning system-wide (see Figure 5e,f at $\phi \approx 0.68$).5

The abundances of hcp-like ($n_{hcp}$) and fcc-like ($n_{fcc}$) spheres are shown in Figure 6 as functions of packing fraction $\phi$. At $\phi \leq 0.65$, the dense partially crystallized HS packings can be realized with quite different abundances of hcp-like and fcc-like spheres. Another important parameter characterizing the local structure is the abundance $N_w$ of spheres having icosahedral-type (5-fold) symmetry (see Figure 4, inset). Here, ico-like spheres are defined as spheres having $q_6 \geq 0.61$. The density dependence of $N_w$ shows that ico-like spheres can exist only in a narrow range of $\phi_c$, and its abundance maximizes at $\phi_c$.

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ϕ_c, the relatively slow increase of \( n_{\text{tot}} = n_{\text{hcp}} + n_{\text{fcc}} \) is mainly due to the emergence of randomly distributed single hcp-like spheres. Around \( \phi \approx \phi_c \), the slopes of \( n_{\text{hcp}}(\phi) \) and \( n_{\text{fcc}}(\phi) \) increase significantly. At \( \phi \approx 0.66 \), the abundance of the fcc-like spheres is equal to that of the hcp-like spheres (\( n_{\text{fcc}} \approx n_{\text{hcp}} \)). Additionally, the abundance of spheres having number of contacts \( N_c = 12 \) is plotted in Figure 6, as one more sensitive indicator of the crystallization of a dense HS. The relative cumulative spectrum of cluster mass is plotted in the inset of Figure 6, showing that this distribution becomes wider as the density increases.

**DISCUSSION AND CONCLUSION**

The above results illustrate a sharp first-order-like transition at \( \phi_c \) between disordered (frictional) packings and partially ordered packings. Amorphous frictionless packings only exist at a single density \( \phi_c \); below \( \phi_c \), the packings are unstable unless they are frictional (and the frictional packings are disordered); above \( \phi_c \), the packings are partially ordered. On the other hand, multiple amorphous frictionless states have been found in other simulations, which supports the mean-field theoretical prediction that amorphous jammed packings should exist in the interval (so-called J-line) \( \phi \in [\phi_{\text{th}}, \phi_{\text{GCP}}] \). We stress that this apparent contrast is due to the presence of crystallization: If the nucleation rate is slow enough, such as in polydisperse or large

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**Figure 5.** Distributions of hcp and fcc clusters over the space at different \( \phi \) values: \( \phi \approx 0.65 \) (a, b), \( \phi \approx 0.66 \) (c, d), and \( \phi \approx 0.68 \) (e, f). Particles are color-coded by the mass of the cluster (in the unit of the mass of a single sphere). At \( \phi \approx 0.65 \), single hcp-like spheres dominate. At \( \phi \approx 0.65 \), three-dimensional local clusters of both hcp- and fcc-like particles are observed. Further densification of HS results in a structural transition: the 3D local clusters transform into global and planar layers (e, f).
dimensional systems, then crystallization is suppressed and dense amorphous packings can be obtained by slow compressions; while in 3D monodisperse systems, the nucleation process is so fast such that any slow compression would result in partial crystallization. Combined with the mean-field prediction, our results suggest two possible scenarios for 3D monodisperse packings: (i) \( \phi_c < \phi_{th} \), therefore, dense amorphous packings \( \phi > \phi_{th} \) are hidden by crystallization; (ii) \( \phi_{th} \lesssim \phi_c \), however, the difference between \( \phi_{th} \) and \( \phi_c \) is very small, such that the amorphous packings in the range \( [\phi_{th}, \phi_c] \) are difficult to detect on the basis of the present numerical accuracy. Further studies are required to test these two scenarios.

To conclude, we have studied structural properties of dense hard spheres in the vicinity of the Bernal limit. The spatial and bound order parameters and the abundances of hcp-, fcc-, and ico-like particles all indicate a sharp disorder–order phase transition at \( \phi_c \). Finally, we find that at packing fraction \( \phi \approx 0.68 \) an additional structural transition occurs: the 3D-like shape of solid-like crystalline clusters changes to a planar-like structure.

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