Structural properties of dense hard spheres near random close packing

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The structural properties of dense random packings of identical hard spheres (HSS) are investigated by using large scale simulations. The bond order parameter method is used to obtain detailed information on the local orientational order of the HS system at different packing fractions \( \phi \), in the range between \( \phi \approx 0.53 \) and \( \phi \approx 0.72 \). The probability distribution functions of the spheres versus different \( q_l \) are used to construct new measures, characterizing the crystallization of the system. Our results show that behind the Bernal limit the crystalline clusters transform into the global three-dimensional crystalline structure, which, upon further densification, transforms into alternating planar layers formed by different lattice types.

The model of hard spheres (HS) is of fundamental importance in condensed matter physics and material science since it successfully reproduces the essential structural properties of liquids, crystals, glasses, colloidal suspensions and granular media \cite{1,2}. Structural changes of the HS system have been observed when a packing is densified above the density of random close packing (RCP) \( \phi_c \approx 0.64 \) (see, e.g. \cite{3,4}). A new order parameter, based on the cumulative properties of spheres distribution over the rotational invariant \( w_l \), was proposed in \cite{5} to identify this structural changes. Random arrangement is transferred to partial crystallization across RCP, and two lattice types (fcc and 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 test previous findings, and to further explore the structural properties of the transition at RCP in more details in comparison with previous studies \cite{3,4}, based on larger scale simulations. In particular, we take a large set of packings composed of \( N = 64 \times 10^4 \) identical spheres with periodic boundary conditions, generated using modified Lubachevsky-Stillinger (LS) algorithm \cite{5}. The packing fraction depends on the compression rate as slower compressions result in denser packings. The packings obtained from LS algorithm are then used as initial configurations to generate mechanically stable jammed packings of particles interacting with Hertz normal forces. When \( \phi < 0.64 \), Mindlin frictional forces are added to stabilize the packings. More details of the numerical algorithm are described in Refs. \cite{4}. The corresponding packing fractions vary in the range \( \phi \approx 0.53 - 0.72 \). The range includes the random close packing state at \( \phi_c \approx 0.64 \) (Bernal limit) \cite{6}.

To define the local structural properties of the system we use the bond order parameter method \cite{7}, which has been widely used in the context of condensed matter physics \cite{7,8}, HS systems \cite{10,11}, complex plasmas \cite{16,21}, colloidal suspensions \cite{22,23}, granular media \cite{24} etc. In this method the rotational invariants (RIs) of rank \( l \) of both second \( q_l(i) \) and third \( w_l(i) \) order are calculated for each sphere \( i \) in the system from the vectors (bonds) connecting its center with the centers of its \( N_{nn}(i) \) nearest neighboring spheres:

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

\[
w_l(i) = \sum_{m_1,m_2,m_3} \left[ \begin{array}{ccc} l & m_1 & m_2 \\ m_2 & m_3 \\ m_1 \\ \end{array} \right] q_{lm_1}(i) q_{lm_2}(i) q_{lm_3}(i),
\]

where \( q_{lm}(i) = N_{nn}(i)^{-1} \sum_{j=1}^{N_{nn}(i)} Y_{lm}(\mathbf{r}_{ij}) \). These spherical harmonics and \( \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \) are vectors connecting centers of spheres \( i \) and \( j \). In Eq. (2) \( \left[ \begin{array}{ccc} l & m_1 & m_2 \\ m_2 & m_3 \\ m_1 \\ \end{array} \right] \) are the Wigner 3j-symbols, and the summation in the latter expression is performed over all the indexes \( m_1 = -l, ..., l \) satisfying the condition \( m_1 + m_2 + m_3 = 0 \). In 3D the densest possible packings of identical hard spheres are known to be face centered cubic (fcc) and hexagonal close-packed (hcp) lattices (\( \phi_{fcc} = \phi_{hcp} = \sqrt{2\pi}/6 \approx 0.74 \)). Presence of spheres having icosahedral (ico) symmetry is also possible in the dense HS system. To detect these structures we calculate the rotational invariants \( q_4, q_6, w_4 \) and \( w_6 \) for each sphere using the fixed number of nearest neighbors \( N_{nn} = 12 \) \cite{25}. A sphere whose coordinates in the 4-dimensional space \((q_4, q_6, w_4, w_6)\) are sufficiently close to those of the ideal fcc (hcp, ico) lattice is counted as fcc-like (hcp-like, ico-like) sphere. By calculating the bond order parameters it is easy to identify also disordered (liquid-like) phase (for instance,
FIG. 1: (Color online) Probability distribution functions (PDFs) of the rotational invariant $q_6$ (a) and $q_4$ (c) and $w_6$ (b) and $w_4$ (d)) for different packing fraction $\phi$. Values of the bond order parameters for ideal lattice types are also indicated. Cumulative distributions (normalized to unity) are shown by dashed line of the same color; the distributions are much less noisy than PDFs. Insets (from top to bottom) show HS distributions over the cubic box at different packing fraction $\phi \approx 0.65$, 0.66, 0.68, respectively. The spheres are color-coded by $q_6$ value to visualize disordered liquid-like (blue), hcp-like (green) and fcc-like (red) phases. Number of particles in the box is $N = 64 \times 10^3$. 
such spheres have mean bond order parameter $q_{6}^{\text{liq}} \simeq N_{nn}^{-1/2} \simeq 0.29 \ll q_{6}^{\text{fcc/hcp/ico}}$. By varying number of nearest neighbors $N_{nn}$ and rank $l$ of bond order parameter it is possible to identify any lattice type (including quasicrystalline particles and distorted hcp/fcc/ico modifications) existing in the system of particles (e.g., by using $N_{nn} = 8$ and 14 it is easily to identify the first and the second shells of the body centered cubic (bcc) lattices, etc.). We note, that the bond order parameters $w_{l} \propto q_{l}^{3}$, so, in general, the parameters $w_{l}$ are much more sensitive to the local orientational order in comparison with $q_{l}$.

Figure 1 shows the probability distribution function (PDF) of the rotational invariants of second $q_{4}$, $q_{6}$ and third $w_{4}$, $w_{6}$ orders, for different packing fraction $\phi$ covering both liquid-like and crystalline states of HS. Densification of the HS, as clearly seen in the Figure 1 results in appearance of the crystalline particles in the vicinity of the Bernal limit (RCP). Cumulative distributions (shown by dashed lines) are also plotted; those can be used to define the number density of hcp/fcc/ico-like spheres in the system (and disordered solid-like spheres as well). Such cumulative distributions being much more smoothed than corresponding PDFs are proposed to create the order parameters characterizing the phase state of the HS system.

It has been shown recently [20] that the cumulative distribution function of the form

$$\hat{W}_{6}(x) \equiv \int_{-\infty}^{x} n(w_{6})dw_{6}$$

(3)

is an extremely sensitive measure of the structural order in the system (in Ref. [20] the function $\hat{W}_{6}(x)$ was introduced for the first time to quantify the solid-liquid transition in confined 3D Yukawa system). Here $n(w_{6})$ is the PDF of spheres over the rotational invariant $w_{6}$ normalized to unity. The relevant order parameter is the position of the half-height of the cumulative distribution $w_{6}^{\text{hh}}$, such that $\hat{W}_{6}(w_{6}^{\text{hh}}) = 1/2$. Here, the order parameter is used to identify the onset of crystallization in the randomly packed HS system.

Figure 2 shows the dependence of the order parameter $w_{6}^{\text{hh}}$ and the mean value of $q_{6}$ [defined as $\langle q_{6} \rangle = ...$]
squares corresponds to the case with $N = 64 \times 10^3$ spheres. The very good agreements between different system sizes are clearly seen – it suggests that HS consisting of $N = 10^4$ spheres well reproduces the global structural properties of the HS system. Explosive-like growth of the order parameter $u_{6\phi}^{hh}$ at $\phi > \phi_c$ reflects the appearance of crystalline order (hcp-like and fcc-like spheres). This proves the usefulness of this structural measure to locate the onset of crystallization, as demonstrated here in the context of randomly packed HS systems. The dependence of the HS system results in strong oscillations of $q_{6\phi}$, which start at $\phi \approx 0.68$ and suggest another transition $RCP \rightarrow GCP$. Geometry gives a simple explanation of such an oscillatory behavior: The point is that the hcp and fcc crystal structures are characterized by quite different values of the parameter $q_6$ (for ideal hcp and fcc lattices $u_{6\phi}^{hcp} \approx 0.48$ and $u_{6\phi}^{fcc} \approx 0.57$). Dense HS packings can be apparently realized (for a given $\phi$) with significantly different relative quantity of hcp and fcc phases. This explains the oscillations. Inset in Fig. 2 shows another important measure characterizing structure of HS near RCP: number density $N_{ico}$ of spheres having icosahedral symmetry (ico-like or fivefold spheres) versus packing fraction $\phi$. It shows that ico-like spheres can exist only in a narrow range of parameter $\phi$: at low $\phi$ number of ico-like spheres is exponentially small; densification of HS above $\phi \approx 0.66$ results in nearly disappearance of the ico-like spheres. This suggests that the abundance of ico-like spheres can be used as a measure, characterizing HS crystallization.

Cluster analysis of the arrangements of hcp-like and fcc-like spheres reveals another interesting structural property of dense HS packings. Figure 4 shows how the distribution and the shape of clusters composed of hcp and fcc-like spheres vary upon the densification of the system. For relatively low volume fractions $\phi < 0.65$ (Fig. 4a, b)), ico-like clusters consist of only few spheres. Increase of $\phi$ results in the appearance of several big (containing few tens of spheres) both hcp and fcc-like clusters. A typical cluster has a complicated 3D shape (Fig. 4c, d) for $\phi \approx 0.66$). Eventually, nuclei of fcc-like and hcp-like clusters transform into a global crystalline structure occupying most of the system volume. Further increase in $\phi$ leads to a structural change: a transition from 3D clusters to 2D layers composed of fcc-like and hcp-like spheres occurs which is in full agreement with results of 3.

The relative numbers of spheres in hcp-like ($n_{hcp}$) and fcc-like ($n_{fcc}$) states are plotted in Figure 4 as functions of $\phi$. For $\phi < \phi_c$ the relatively slow increase of $n_{tot} = n_{hcp} + n_{fcc}$ with $\phi$ is associated with emergence of single hcp-like spheres, which are nearly randomly distribute over the system volume. At $\phi \approx \phi_c$ the slopes of $n_{tot}(\phi)$ and $n_{fcc}(\phi)$ are drastically increase. The number of fcc-like spheres reaches that of the hcp-like spheres ($n_{fcc} \approx n_{hcp}$) at $\phi \approx 0.66$, where transition from hcp-dominated to fcc-dominated packing occurs. Additionally, the abundance of spheres having number of contacts $N_c = 12$ is plotted in Figure 4 making this measure to be one more very sensitive indicator of the crystallization of a dense HS. Inset in Figure 4 shows the relative cumulative spectrum of hcp (fcc)-like (red and green line, respectively ) clusters as a function of the cluster mass at different $\phi$ values. The hcp/fcc spectrum near the RCP ($\phi \sim 0.65$) reveals already mentioned features: only small clusters consisting of few spheres are present in the HS system. As the density increases, larger clusters appear. This observation is consistent with the classical nucleation process 20: the denser packings are more “supercooled” before falling out of equilibrium, therefore they have lower free energy barriers to form large clusters.

The above results illustrate a sharp first-order like transition 4 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. In contrast, multiple amorphous frictionless states have been found in other simulations 21,22, which supports the mean-field theoretical prediction that amorphous jammed packings should exist in the interval (so-called J-line) $\phi \in [\phi_{hh}, \phi_{cJ}]$ 11. The key point here is whether crystallization is present or not. If the nucleation rate is slow enough, such as in polydisperse 22 or large dimensional systems 23, then crystallization is suppressed and the J-line is well observed. In the present case we have employed monodisperse sphere packings in three dimensions. In such systems, the nucleation rate is relatively fast, which prevents any slow compression to produce dense amorphous packings. As a result, we find any frictionless packings above $\phi_c$ are partially crystallized as revealed by measures of order parameters. Combined with the mean-field prediction, our results suggest two possible scenarios in 3D monodisperse packings: (i) $\phi_c < \phi_{hh}$, therefore amorphous packings are hidden by partial crystallization; (ii) $\phi_{hh} \lesssim \phi_c$, however the difference between $\phi_{hh}$ and $\phi_c$ is small and difficult to detect based on present numerical accuracy. Further test of the subtle differences between these two scenarios may require even larger-scale simulations.

To conclude, we have demonstrated that the order parameter, based on the cumulative distribution of spheres over the values of the rotational invariant $w_6$ is a very sensitive measure to describe the onset of crystallization in the system of randomly packed hard spheres. The proposed order parameter is also especially convenient indicator of the
appearance of hcp, fcc and ico-like crystalline particles in the system. It has been shown, that abundance of icosahedral particles decrease drastically after RCP limit, making the measure to be one more indicator of the HS system crystallization. We used this to investigate how the relative distribution between hcp and fcc arrangements varies with increasing the sphere packing fraction. Finally, we observed that at $\phi \approx 0.68$ the structural transition occurs: The essentially three dimensional shape of the global crystalline aggregate changes to planar (layered) structure.

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FIG. 3: (Color online) Distribution of hcp and fcc clusters over the space at different φ values: φ ≃ 0.65 (a, b), φ ≃ 0.66 (c, d) and φ ≃ 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 low φ single hcp-like spheres dominate (a, b). The densification leads to the formation of large 3D clusters of both hcp and fcc-like spheres. Eventually, clusters of fcc-like and hcp-like spheres transform into a global crystalline structure. Further densification results in the structural transition, when essentially 3D shape of this global crystalline structure changes to planar 2D layers formed by fcc-like (shown in the figure) and hcp-like spheres.
FIG. 4: (Color online) Abundance of hcp-like (red) and fcc-like (green) spheres versus the packing fraction $\phi$ as seen from detailed simulations of HS systems. For moderate packing fractions ($\phi \leq \phi_c$), the increase of crystalline particle with $\phi$ is due to the appearance of a single hcp-like spheres. Results of large scale simulations with $N = 64 \times 10^3$ spheres are shown by squares (orange and green colors correspond to hcp and fcc-like spheres). The dependencies show pretty well agreement between the cited HS systems. Additionally, the abundance of spheres having number of contacts $N_c = 12$ is plotted by blue square, making this measure to be one more sensitive indicator of the crystallization of dense HS systems. Inset shows the relative cumulative spectrum of hcp (fcc)-like (red and green line, respectively) clusters versus its mass at different $\phi$ values: $\phi \simeq 0.68$ (solid, triangles), $\phi \simeq 0.66$ (dashed, gradients) and $\phi \simeq 0.65$ (solid, circles).