Nucleation and crystal growth in sheared granular sphere packings

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We investigate the nucleation of ordered phases, their symmetries, and distributions in dense frictional hard sphere packings as a function of particle volume fraction $\phi$, by imposing cyclic shear and constant applied pressure conditions. We show, with internal imaging, that the nucleating crystallites in the bulk consist of $10^{60}$ spheres with hexagonal close packed (hcp) order and non-spherical shape, that are oriented preferentially along the shear axis. Above $\phi = 0.62 \pm 0.005$, crystallites with face centered cubic (fcc) order are observed with increasing probability, and ordered domains grow rapidly. A polycrystalline phase with domains of fcc and hcp order is observed after hundreds of thousands of shear cycles.

The nucleation and growth of crystals from initially disordered packings is fundamental to material science, and important to self-assembly of ordered solids from discrete elements. It is well known that thermal frictionless hard sphere systems undergo a glass transition above a volume fraction $\phi_g \sim 0.58$, and crystallization above $\phi_g$ upon application of shear [1, 2]. Experiments with colloidal systems have shown the nucleating crystal to be non-spherical, containing about a hundred particles, with a random hexagonal close packed (rhcP) structure [3].

Here, we consider the development of ordered phases in disordered frictional granular sphere packings. Granular materials are athermal and energy has to be input continuously to rearrange particles. Furthermore, friction forces alter the stability criterion at contact compared with frictionless case, reducing the number of contacts required for stability from 6 to 4 [4]. Both these facts make it difficult to directly apply what has been learned in frictionless hard sphere systems to granular systems. While simulations have shown that friction can affect packing [5] and increase the volume fraction at which disorder can persist in sheared granular flows to well above those seen in frictionless systems [6], ordered packings have been observed upon application of prolonged periods of shear in granular spheres [7, 8]. However, nucleation of ordered phases, their symmetry during nucleation, and evolution upon prolonged shear need to be investigated to gain a deeper understanding of crystallization in granular systems.

We address these issues with experiments using a cyclic shear apparatus which is amenable to three dimensional visualization with a refractive index matching technique. While this technique has been used recently to examine perturbations to disordered packing [9, 10], we perform the experiments over unprecedented long periods to observe development of crystals. It is noteworthy, that it is difficult to eliminate the gravitational field in three dimensional granular packings, and implement constant volume conditions. Therefore, we do the experiments under constant pressure conditions to have the simplest prescribed conditions. In spite of the many differences, we find remarkable similarity in the development of order in our experiments on granular spheres when compared with those reported in colloidal systems [3].

A schematic diagram of the shear cell and the central region selected for analysis. (b-c) Transversal view of the shear cell 10mm from the top of the system: the initial packing, before applying shear deformations (b), and after $5 \times 10^5$ shear cycles (c).

FIG. 1. (a) The volume fraction as a function of shear cycle number measured inside the viewing volume (red/grey) and in the entire cell (black). Inset: schematic diagram of the shear cell and the central region selected for analysis. (b-c) Transversal view of the shear cell 10mm from the top of the system: the initial packing, before applying shear deformations (b), and after $5 \times 10^5$ shear cycles (c).
greater than the weight of the grains and is observed to
remove the effects of gravitational gradients on the ob-
served packings. A refractive index matched interstitial
liquid [11] with a small amount of fluorescent dye is il-
luinated with a laser light sheet. The particles appear
dark in contrast and are imaged with a digital camera
from an orthogonal direction. A stack of images is then
obtained by linearly translating the plane of illumination
along with the camera to measure the position of all par-
ticles with a precision of 0.1d in three dimensions using
standard image processing. The side walls of the cell are
slowly tilted between ±π/36 radians to quasi-statically
shear the system and avoid any lubrication effects due
to the interstitial liquid. A more detailed description of
the apparatus and the imaging technique can be found
in Ref. [10].

The volume fraction of the glass beads \( \phi \) in the entire
system is obtained by measuring the height of the top
surface of the cell as a function of shear cycle \( N_{sc} \) ap-
plied over a 4 month period [12]. The volume fraction is
observed to increase well above the random close packing
fraction \( \phi_{rcp} \) of 0.637 [13] over hundreds of thousands of
shear cycles. A cross sectional image of the initial random
packing and the polycrystalline phase which develops af-
fter \( N_{sc} = 5 \times 10^5 \) is shown in Fig. 1(b) and Fig. 1(c),
respectively. While ordered regions appear aligned near
the boundaries, crystalline phases in the central regions
are not aligned with the boundary. We simultaneously
recorded a stack of images in a 44d \( \times 7d \times 17d \) volume in
a central region of the cell \( 6d \) from the front wall and the
bottom of the cell as indicated in Fig. 1(a) to avoid direct
boundary effects. Figure 1 shows that \( \phi \) obtained in this
region follows, up to \( N_{sc} \sim 1000 \) the overall trend except
with larger fluctuations due to the smaller size of the ob-
servation window. For the next \( N_{sc} \sim 100000 \) the volume
fraction of the entire cell is systematically larger than in
the central region. This difference can be explained by
the fact that the boundary induced crystallization starts
to grow inside the packing. At \( N_{sc} \sim 100000 \) a significant
increase in the value of the packing volume fraction in the
central region can be observed which coincides with the
beginning of the crystal growth in bulk, as will be dis-
scussed later in the text. After half million shear cycles
the packing volume fraction of the entire cell and in bulk
converge to similar value as the entire packing becomes
a polycrystalline structure.

Fig. 2(a) shows the radial density distribution function
\( g(\vec{r}) \) as a function of distance \( r \) to characterize the develop-
ment of spatial order with \( \phi \). In the case of a random
system (liquid or amorphous solid) there is only short
range order and therefore only the nearest coordination
shells are visible, while for a crystalline solid, \( g(\vec{r}) \) exhibit
sharp peaks. Fig. 2(a) shows that the system remains in a
disordered state until \( \phi \sim 0.62 \), when a small shoulder in
the second peak of \( g(\vec{r}) \) signals the appearance of ordered
domains [14]. The bond orientation order parameter, \( Q_l \)
is typically used to characterize the appearance of global
hexagonal order and is obtained using [15, 16]:

\[
Q_l = \left( \frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} |Y_{lm}(\Theta(\vec{r}), \Phi(\vec{r}))|^2 \right)^{1/2},
\]
with \( l = 6 \). Here, \( Y_{lm} \) are the spherical harmonics, \( \Theta(\vec{r}) \)
is the polar angle, \( \Phi(\vec{r}) \) is the azimuthal angle, \( \vec{r} \) is the vector between a particle and its pair, and the angled brackets indicate averaging particle pairs. If averaging is performed over all pairs of particles in the system, then one obtains a measure of the global orientational order \( Q_{l,global} \) in the system. Whereas, if the averaging is performed over nearest neighbors - defined as particles within the distance to the first minima in \( g(\vec{r}) \) - then a local measure of orientational order \( Q_{l,local} \) is obtained. For disordered structures, \( Q_l \) goes as the inverse of the number of particle pairs used in the average and is small [17]. But, its value becomes significantly larger for ordered sys-
tems and reaches 0.575 for a fcc crystal [17]. In Fig. 2(b),
we plot global \( Q_{6,global} \) as a function of \( \phi \) averaged over a
small 0.05 interval of \( \phi \) to reduce noise. The value of
\( Q_{6,global} \) is close to zero for packing fractions less than
\( \phi = 0.62 \), but is then observed to increase sharply consis-
tent with the onset of crystallization. Both these global
measures show that an ordering transition indeed occurs
in our granular system around the random close packing
fraction \( \phi_{rcp} \).

To identify the development of crystallites and their
symmetry, we calculate the local bond orientation or-
ter \( Q_{l,local} \) and \( Q_{6,local} \) for each particle in the ob-
servation window. Making a scatter plot of these two
measures helps us distinguish clearly if hexagonal
close packed (hcp) or face centered cubic (fcc) symme-
try are present (see inset to Fig. 2(b)). Fig. 3 shows
the points are broadly distributed before application
of shear, but clearly cluster around the values expected

\[
\text{Fig. 2. (a) A curtain plot of the radial distribution function } g(\vec{r}) \text{ as a function of normalized distance } r/d \text{ for several volume fractions. Above } \phi = 0.63 \text{ several peaks corresponding to a fcc/hcp lattice become visible. (b) Plot of } Q_{6,global} \text{ versus } \phi. \text{ The sudden increase in } Q_{6,global} \text{ value indicates the beginning of the crystallization. Inset: the layers indicated by A,B,C repeat with different periods for hcp and fcc symmetries.}
\]
for fcc and hcp structure for \( N_{sc} = 5 \times 10^5 \). Lack of any other peaks also implies that no other type of crystalline order develops in our system. In subsequent analysis, we choose a narrow range \( 0.08 \leq Q_{4,local} \leq 0.16 \), \( 0.46 \leq Q_{6,local} \leq 0.5 \) to label hcp, and \( Q_{4,local} \leq 0.175 \), \( Q_{6,local} \leq 0.54 \) to label fcc regions.

Figure 4 shows particles in the mid-plane of the packings with different shades depending on if they belong to fcc or hcp configuration. (The entire sequence is shown as a movie in the supplementary documentation.) It can be noted that even for \( \phi < \phi_{hcp} \), small hcp clusters are distributed inside the system. These ordered clusters were initially observed to appear and disappear quite frequently, but become more stable with increasing \( \phi \). By following the crystallites from one shear cycle to the next, we estimated the critical size of nuclei to be 10 - 60 particles. Remarkably our results are similar to experimental studies of thermal colloidal suspensions [3], even though that study was conducted at constant volume with thermal

frictionless hard spheres.

To test if shear has influence on shape and orientation of the nucleating clusters, we calculate the moment of inertia tensor associated with each cluster of size \( 5 \leq N \leq 50 \):

\[
I_{jk} = \sum_{i=1}^{N} (\vec{r}_i^2 - x_{i,j} x_{i,k}).
\]

Where \( N \) is the number of particles in a cluster, \( i \) labels the particles, \( j,k \) label the components of \( \vec{r} \), the vector from particle \( i \) to the cluster’s center of mass. The square root of the eigenvalues of the moment of inertia tensor denoted by \( \lambda_{1,2,3} \) are shown in Fig. 5(b). For a spherical nucleus these values should be identical. Because the principal radii of the ellipsoid fitting the cluster is inversely proportional to \( \lambda_{1,2,3} \), we find that the average shape of the nuclei is non-spherical, with the principal radii being roughly in a 2:1:1 ratio (see Fig. 5(b)). The eigenvectors of the moment of inertia tensor then allow us to determine the orientation of the nuclei. We plot the histogram of the polar angle \( \theta \) from the positive z axis (shear gradient direction), and the azimuthal angle \( \phi \), in xy plane from the x axis (shear direction), made by the longest axis of the ellipsoid, in Fig. 5(c), respectively. The peaks are observed at \( \theta = \pi/2 \) and \( \phi = 0 \), show-
In order to have an estimate of the scale of the crystal domains in our experiments, we calculate the correlation length corresponding to the size of the observed domains of fcc and hcp phases [24]:

$$\xi = \frac{2 \sum R_g^2(s) s^2 n_s}{\sum s^2 n_s}.$$  \hfill (3)

Here \(n_s\) is the number of clusters of size \(s\) and \(R_g(s)\) is their radius of gyration. Fig. 6(b) shows that the correlation length of the fcc clusters increases more rapidly than the correlation length of the hcp clusters above \(\phi_{hcp}\). Thus we conclude that the two phases, fcc and hcp, are well separated in our system and distinct from a rhcp phase, in addition to the observation that the fcc phase becomes more abundant. A similar evolution has also been observed in numerical simulations with hard spheres as well [25].

In summary, we have shown with delicate experiments that sheared granular systems undergo homogeneous nucleation in addition to inhomogeneous nucleation at sidewalls. We measured the size and the symmetry of the ordered phases and estimated the surface tension of the nucleating crystallites in athermal frictional hard sphere systems for the first time, and showed the influence of shear on the shape and orientation of the crystallites. The process of nucleation is also surprisingly similar to the one observed in computer simulations [19] and experiments [3] on thermal colloidal hard sphere suspensions, suggesting that the development of crystallization in hard sphere systems is far more universal than previously anticipated.

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The liquids have a density of \(1.0 \times 10^3 \text{kg m}^{-3}\) and viscosity of \(2.2 \times 10^{-2}\) Pa s, and were obtained from Cargille Laboratories.

See Supplemental Material at [URL will be inserted by publisher] for a movie of the development of the crystalization in a slice inside the granular packing located 10d from the front wall (M1) and a 3D reconstruction of the same region (M2) after particle tracking.


