Nucleation of athermal hard spheres

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We present an experiment with packings of macroscopic spheres that model disordered and particulate systems and provide insight into the less accessible atomistic world. Cyclically shearing a packing of frictional spheres, we observe a first order phase transition from a disordered to an ordered state. The ordered state consists of crystallites of mixed FCC and HCP symmetry that coexist with the amorphous bulk. The transition, initiated by homogeneous nucleation, overcomes a barrier at 64.5% volume fraction. Nucleation consists predominantly of the dissolving of small nuclei and the growth of nuclei that have reached a critical size of about ten spheres. Our results indicate that classical nucleation theory is not applicable if the nucleation barrier is identified with a depleted region at the nucleus interface.

PACS numbers: 64.70.ps, 61.43.Gt, 64.60.Q-

Packings of spheres show interesting features such as phase transitions between disordered and ordered states, and can be useful in the study of amorphous atomic configurations [1]. Examples include thermal colloidal packings [2–5], macroscopic athermal packings of hard spheres [1, 6–18], and simulations of the mathematical hard sphere model [19–27]. The behavior of such systems is determined by the fraction of space filled by the spheres, their packing fraction $\phi$.

The hard sphere model exhibits an entropically driven first order phase transition. Disordered fluid states are observed below the freezing density of $\phi = 0.495$ and crystalline ordered states appear above the melting density of $\phi = 0.545$, with coexistence of the two phases for intermediate densities [23].

Athermal spheres can also be packed in disordered and ordered states. Most experimental bulk protocols for increasing their volume fraction such as vertical shaking [14], centrifugation [4], thermal cycling [12, 13] and sedimentation [15] do not achieve an ordered state from an initial disordered state. The “random close packed state” (RCP) is informally used to describe the highest density state achieved by these methods, with a packing fraction in the range $0.635 < \phi < 0.655$ [18–21], about 15% lower than the densest possible packing of ordered face centered cubic (FCC) or hexagonal close packing (HCP), which both have a volume fraction $\phi = \pi/\sqrt{18} \approx 0.74$ [28].

Ordered clusters of spheres have been observed with a system density $\phi_{\text{global}}$ in the range 0.64–0.74 by multidimensional shaking [8–10], cyclic shear [6, 7], and shear in a Couette cell [11, 16]. By analogy with the freezing-melting transition in the hard sphere model, the emergence of growing crystallites exhibited by athermal spheres can be described in terms of nucleation and a first order phase transition [22, 29]. The homogeneous nucleation and growth of ordered clusters which we report support such a description.

The description of phase transitions in equilibrium statistical mechanics is often enriched by classical nucleation theory (CNT) [30]. The free energy cost required to create an interface between coexisting amorphous and ordered phases gives rise to a free energy barrier. The barrier is a function of the critical nucleus size and consists of a positive quadratic interfacial free energy and a negative third order free energy phase difference. For small clusters the surface energy is significant; small nuclei tend to shrink while large nuclei tend to grow.

In our experiment we compact spheres by shearing. With increasing shear cycles, a well-defined plateau emerges at nucleation/phase transition density $\phi_{\text{global}} = 0.645$; such a plateau was not reported in a previous experiment [6] that used a setup similar to ours. The observed plateau density is in the range of densities associated with RCP [18–21]. Our observations also yield a nuclei growth rate that differs qualitatively from a previous experiment [6]. We cannot identify a nucleation barrier at the nucleus surface in the framework of CNT.

The shear cell is cubical with side length 10.5 cm (Fig. 1(a)). Nucleation from the side walls is suppressed by half-spheres that are glued to the walls at random positions (glue: Vitralit 7562, Panacol). The cell is filled with 49,400 precision BK7 glass spheres of diameter 3 ±0.0025 mm and density 2.51 g/cm$^3$ (size tolerance given by manufacturer, Worf Glaskugeln GmbH).

The top plate applies a pressure of 2.1 kPa on the bed, and the pressure increases downward to 3.1 kPa at the bottom. The cell is sheared by sinusoidally tilting...
The image quality in both layers is comparable. (c) shows a layer much further from the camera. Note that the Shear is produced by periodically oscillating the cell bottom in a slice in the ¶-direction with a period of 2 s. A laser sheet illuminates the cell walls are made of BK-7 optical glass and are index matched with the liquid mixture in a temperature controlled environment (n = 1.5198 ± 0.0001 at λ = 589 nm and T = 22.9 ± 0.1°C). The shearing process is periodically stopped to measure the packing using an horizontally translated vertical laser light sheet (λ=658 nm, P=75 mW). Fluorescent light is imaged simultaneously by the camera (Figs. 1(b,c)). The image slices are combined to form a three-dimensional volume. The measurements presented here are from 618 scans made during a run with 1.955 × 10^6 cycles.

In the course of the two month long run 10% of the spheres escaped from the sample cell through a gap between one of the shear walls and a side wall. This unplanned draining of spheres may have increased the mobility of spheres farther inside the packing, thereby enhancing their crystallization.

Positions of the 20,000 spheres at least 3 diameters from any wall are detected by convolution with a gradient-based template [32]. Then the peak of the correlation map in the (x,y,z) directions is determined with (37,37,30) pixel/diameter resolution using a 3-point Gauss estimator [33]. This yields the positions of all particles. From the pair correlation function we can determine the accuracy to better than 2% of a sphere diameter for 99% of the particles (see Supplemental Material [34]).

For each sphere there is a Voronoi cell consisting of all points closer to that sphere than to any other sphere in the sample (see insets in Fig. 2(a)). φ_{local} is then the ratio of the sphere volume to the volume of its Voronoi cell. The mean volume fraction of the whole sample φ_{global} is given by the harmonic mean of all φ_{local} values [35].

The angular order between spheres sharing a face of their Voronoi cells is characterized by a weighted version of the order parameter, q_{6} [27]. A sphere is called crystalline if it is densely packed and its neighbors are ordered, i.e., φ_{local} > 0.72 and q_{6} is either in the range q_{6}(FCC)=0.575±0.02 or q_{6}(HCP)=0.485±0.02. Other authors suggest different definitions for local order, but our results do not depend qualitatively on the choice of definition or threshold (see Supplemental Material [34]). Crystalline spheres that share a Voronoi face are considered to be part of the same nucleus. The distance of a nucleus to another single sphere or nucleus is given by the shortest distance between the sphere centers.

During densification we observe three distinct regions, as can be seen in Fig. 2(a). The packing starts from a disordered state and compacts approximately logarithmically with time for about 20,000 cycles. The compaction then slows to a stop, and the second region, a plateau (φ_{global} = 0.645), emerges and persists for about 50,000 cycles. Then the first growing nucleus appears, indicating a first order phase transition to the third distinct region. The volume fraction slowly begins to increase as shearing continues, and nuclei increase in number and size but have no preferred orientation of their hexagonal layers; an intermediate state of the system is shown in Fig. 3(a). The first growing nucleus is shown in Fig. 3(b), which illustrates that nuclei fluctuate in shape, size, and crystal symmetry as they grow, as can be seen in the movie in the Supplemental Material [34].

All nuclei start their growth at least 10 sphere diameters distance away from any wall. By the end of the experiment, after two million shear cycles, nuclei with up to ~ 600 spheres are present, and 9% of all spheres are in crystallites, which have FCC or HCP symmetry with approximately equal probability; no icosahedral symmetry was observed.

Histograms of local densities for amorphous packings have a single peak and are approximately symmetrical about that peak, as Fig. 2(b) illustrates. During compaction the peak narrows slightly and shifts to higher densities. Beyond the first order phase transition a second peak emerges at φ_{local} = 0.74, the density of densest
packed arrangements.

The end of the densification plateau is identified by the emergence of a nucleus in the interior region; subsequently all nuclei are tracked for each successive scan. Nuclei with fewer than about ten spheres are found to shrink more often than grow, while growth gradually becomes more probable for nuclei with more than ten spheres, that is, $\Delta \rho = (\rho_{\text{grow}} - \rho_{\text{shrink}}) > 0$, where $\rho$ is the probability to grow or shrink, respectively [3, 6]. $\rho_0$ that defines a nucleus does not shift the critical size at which the difference of the probabilities $\Delta \rho$ becomes positive (see Supplemental Material [34]).

Our main result is the observation of homogeneous nucleation in a system of athermal spheres. The emergence of a plateau at a well-defined packing fraction, $\phi_{\text{global}} = 0.645$, indicates the onset of a first order phase transition. A previous experiment used a setup similar to ours and observed inhomogeneous nucleation at the cell walls but no nucleation in the interior of the cell [6]. Another experiment used shaking rather than shearing to study compaction, but the evolution of the nucleation dynamics was not analyzed (8, 9, 36) and Supplementary Material in [8]).

Classical nucleation theory (CNT) has been successfully used to interpret packings of thermal hard colloids, where the size of critical nuclei was measured to be 60–160 spheres [3]. We find that a similar approach does not work for our results for athermal hard spheres. Our main result with respect to the CNT framework is an interface density larger than the bulk density for nuclei smaller than 20 spheres (Figs. 4(b,c)); hence it is energetically favorable for a nucleus to grow. Therefore, the free energy hypothesis of CNT is in contradiction with the observed negative growth probability of small nuclei (Fig. 4(a)). We conclude that CNT seems to be the wrong framework to describe nucleation in athermal sphere packings. Further, we found no qualitative differences if the interfaces of growing and shrinking nuclei were analyzed sepa-

Figure 2. The formation of the crystalline phase shows features of a first order phase transition. (a) Starting from a loose packing, the global volume fraction $\phi_{\text{global}}$ increases logarithmically with the number of shear cycles until it reaches a plateau at the density $\phi_{\text{global}} = 0.645$. After approximately 70,000 shear cycles, $\phi_{\text{global}}$ increases again due to the formation of crystalline regions inside the sample. The 2D diagrams on the upper left show spheres (blue) and their Voronoi cells (yellow) for cases with Voronoi neighbors that are disordered loosely packed (left) and symmetric densely packed (right). (b) Histograms of local volume fractions reveal the coexistence of crystalline and amorphous regions inside the sample. Below the transition there is only a single peaked distribution, which shifts towards higher densities until the plateau is reached. After the onset of crystallization the previous peak population diminishes and a new peak appears at $\phi_{\text{local}} = 0.74$. The histogram for the plateau is the average of 32 consecutive scans; elsewhere the histogram is the average of 10 scans. Colors in (b) correspond to the colored data points in (a).

Figure 3. (a) This cross section of the cell after $10^6$ cycles shows crystalline regions in the cell interior; the amorphous phase is not shown. The colors of the nucleated spheres indicate crystal type. The wire frame indicates the inner part of the shear cell that is used for evaluation. (b) The nucleus that started to grow first (encircled in (a)) fluctuates in shape and size until a stable seed was reached at about $3 \times 10^5$ cycles. (c) Time evolution of the nucleus in (b). A movie in the Supplemental Material [34] illustrates the nucleation in the shear cell.
rately (see Supplemental Material [34]). We also checked for two-step nucleation as recently described for colloidal systems [5], but we found this did not fit our observations of growing nuclei with initial FCC or HCP symmetry without any intermediate phase (Fig. 3).

In conclusion, the present experiment revealed an onset of nucleation growth at 70,000 shear cycles in a system of 49,400 spheres, which indicates that future numerical simulations of sheared packings should extend well beyond a recent study of 2,000 frictional grains cyclically sheared for 2,000 cycles [17].

We thank Markus Benderoth, Thomas Eggers, Tilo Finger, Kristian Hantke, Wolf Keiderling, Udo Krafft, and Vishnu Natchu for technical support and discussions. The project was financed by grants from German Academic Exchange Service (DAAD), German Research Foundation (DFG) STA 425/24 and Cluster of Excellence Engineering of Advanced Materials, and in part by NSF DMS-1509088.

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Figure 4. (a) The growth (shrinking) probability of a nucleus depends on its size: nuclei with about ten or more spheres predominately grow ($\Delta \rho > 0$). (b) Local volume fraction as a function of distance from the surface of a nucleus. Large nuclei (red) show an initial dip [37], but there is no dip for subcritical nuclei (black), and very small nuclei have a minor effect on the surroundings (dashed). (c) The packing density near the surface of a nucleus – in the range in (b) between the vertical dotted lines – is higher for the small nuclei that tend to dissolve than for the large nuclei that tend to grow. The horizontal dashed lines in (b) and (c) indicate the amorphous plateau far away from any nucleus. The symbol size in (a) and (c) indicates the number of examples observed.

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[34] See Supplemental Material at [URL will be inserted by publisher] for a movie and additional evaluations.


[36] For a characterization of the melting process of a crystalline packing using persistent homology see also [10].

[37] Alexey V. Anikeenko and Nikolai N. Medvedev (Laboratory of Molecular Dynamics and Structures, Novosibirsk, Russia) have observed depletion around large nuclei in athermal packings that were generated by Lubachevsky-Stillinger [26] and Jodrey-Tory [24] densification algorithms (private communication).
Supplemental Material: Nucleation of athermal hard spheres

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**movie-spheres-nucleate-Rietz.avi**

The movie shows the nucleation of spheres in the shear cell. For visualization only the spheres that are in a crystalline state are shown in a rotating side view. Color indicates the crystal symmetry. The current state is quantified in the top right by global packing fraction, shear cycle, and the number of crystalline spheres. The end of the plateau in the packing fraction is marked by the advent of the first growing nucleus, which is encircled in the rotating animation and depicted at a constant viewing perspective on the lower right. The wire frame indicates the inner part of the cell, while the green and brown frames are parallel to the shear walls. The bottom of the interrogation volume is cut non-orthogonally because of optical accessibility.

**Precision of sphere coordinates**

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Figure S1. (a) The accuracy of the detected coordinates of the spheres with diameter 3 ± 0.0025 mm is derived from the width of the first peak of the radial distribution function [35]. For ideal monodisperse spheres and known coordinates there would be a step function at a distance of one particle diameter. Under experimental conditions the maximum of the peak is used as the mean particle diameter and the width of the left shoulder characterizes the precision of the sphere coordinates. (b) The overlap length for a given percentile of overlapping contacts. Before counting the number of overlaps, spheres are sorted in increasing order, i.e., the smallest overlaps are first. To exclude outliers the width of the left tail is defined by the largest of the 99% smallest overlaps, the quantile \( q_{99} \). An accuracy of the sphere positions of 2% of a diameter is deduced. The blue range in (a) indicates the overlap by the smallest spheres if only the manufacturer’s size tolerance is considered, i.e., the maximum shoulder width if the coordinates were precisely known. The coordinate error due to size tolerance is negligible compared to the inaccuracy of the detection method. The evaluation includes \( 2.45 \times 10^6 \) calculated sphere coordinates.
No qualitative influence of different thresholds for crystal classification

Figure S2. Combinations of different thresholds for $q_6$ and $\phi_{\text{local}}$ do not change the general picture of preferred dissolution of nuclei with fewer than approximately ten spheres. In this paper spheres are classified as crystalline if $\phi_{\text{local}} > 0.72$ and $\Delta q_6 < 0.02$, i.e., if $q_6$ is either in the range $q_6(\text{FCC})=0.575\pm0.02$ or $q_6(\text{HCP})=0.485\pm0.02$ (circle symbol). The rotationally invariant parameter $q_6$ is used in the literature to characterize the local order of a sphere by considering the relative positions of its surrounding particles [27]. The form of $q_6$ we use weighs neighbors by the area of the Voronoi faces that they share with the central sphere [27]; thus close neighbors are more influential than distant ones. Symbol size indicates number of observations.

Figure S3. Combinations of different thresholds do not change the general picture of an absence of depletion zones around subcritical nuclei. The red solid line corresponds to the parameter used in the paper.
No qualitative influence of a different crystal definition

Figure S4. The results do not depend on the selected definition of local crystallinity as shown here. In addition to $q_6$ crystallinity can also be geometrically characterized by comparison of a given Voronoi cell with the Voronoi cells for FCC and HCP [19]. For comparison a rotationally invariant fingerprint is calculated from the face normals of a single Voronoi cell. A sphere has either FCC or HCP symmetry if the difference of their fingerprints is below a threshold, $\Delta_{\text{FCC,HCP}}$. Symbol size indicates number of observations.

Figure S5. Selection of a different definition for local order checked for two thresholds does not yield in a qualitative change of properties at the nucleus interface.
Influence of bin size on interface behavior

Figure S6. Influence of bin size on $\phi_{\text{local}}$ at the nucleus interface. Left column: bin size 0.5 diameter, as used in paper; right column: bin size 0.01 diameter. The bin step is always 0.005 diameter. The number density at higher resolution is a variant of the radial distribution function. The pronounced peaks at $\sqrt{2}$, $\sqrt{3}$, and 2 diameters correspond to the elementary planar distances illustrated on the lower right in (c).
No qualitative difference in the comparison of growing and shrinking nuclei

Figure S7. The nuclei are split in groups of growing and shrinking nuclei. There is no qualitative difference in $\phi_{\text{local}}$ at the nucleus interface.