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Crystallisation in a Granular Material

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Abstract. The athermal and dissipative nature of packings of grains is still challenging our understanding of their compaction as well as their crystallisation. For instance, some beads poured in a container get jammed in random disordered configurations, which cannot be denser than 64%, the random closed packing (RCP) limit. Remarkably it has been suggested that the RCP bound is saturated with dense patterns of beads aggregated into polytetrahedral structures. Yet when a suitable vibration is applied, a packing of beads might start to order and some regular patterns appear.

We present new experiments on the crystallisation of the packing of beads. By extending tapping techniques, we have obtained packings with volume fractions ϕ ranging from the RCP to the crystal ($\phi = 0.74$). Computing tomography has been used to scan the internal structure of large packings (≈200,000 beads). Voronoi and Delaunay space partitions on the grain centres were performed to characterise the structural rearrangements during the crystallisation. This allows us to describe statistical properties of the local volume fluctuations and the evolution of the densest patterns of beads.

In terms of statistical description, a parameter based on the volume fluctuations discloses different regimes during the transition. In terms of geometry, we confirm that polytetrahedral dense clusters are ubiquitous at the RCP. We describe some intrinsic features of these clusters such as rings of tetrahedra and show how they disappear as the crystal grows.

This experiment enlightens how an athermal system jammed in a complex frustrated configuration is gradually converted into a periodic crystal.

Keywords: granular matter, tomography, statistical geometry, topology
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A packing of spheres is a puzzling material which can have a stable amorphous structure, yet when this disordered assembly is sheared or vibrated it may massively crystallize.

Below the limit of RCP, a packing is in a disordered state in which locally dense configurations of spheres can coexist with loose arrangements [1]. In this regime, compaction under gentle vibrations is extremely slow, in a way reminiscent of the relaxation observed in glass transition [2], and besides the system remains trapped in a disordered state. To overcome the RCP barrier, stronger vibrations have to be applied and the packing starts crystallising. The growing crystalline structure is shaped by the competition between the input of external energy fluxes and the dissipation at the grain contacts. Numerous experiments have reported analogies between this out of equilibrium crystallisation and a thermodynamic transition [3, 4]. An entropic mechanism driving this ordering despite the highly dissipative context is still unknown [3].

As a packing crystallises, it undergoes major grain scale rearrangements. A clear geometrical description of these rearrangements represents a first step towards the elaboration of a statistical framework for granular crystallisation [5, 6]. Such an approach relies on our ability to find relevant patterns in disordered packings, and then to describe their evolution as the system gets denser to eventually crystallise.

Here we follow Bernal's pioneering effort in describing dense packings geometry [5]. He first noticed the predominance of local tetrahedral configurations in dense packings. Moreover he described the propensity of these tetrahedra to pack via their triangular faces to form dense *polytetrahedral* aggregates [5]. These aggregates cannot tile periodically the space, i.e: they are *geometrically frustrated* patterns [7]. In recent computer models [8], it was observed that the RCP state is saturated with dense polytetrahedral clusters, such that any further densification involves the presence of crystalline configurations. Our experimental study describes quantitatively these polytetrahedral structures and their fate beyond the RCP limit.

Advances in X-ray tomography have made grain based description of granular packing possible with an unprecedented level of accuracy(Fig 1, [1]). To describe the granular internal structure, we here use two of the most common space partitions:

- the Voronoi partition where the bead and the surrounding space closest to its center define the elementary brick. The Voronoi cell is directly associated to the local packing fraction as it is wrapped around an entire bead (Fig.1a).

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- the Delaunay partition which is based on local simplices (or irregular tetrahedra) built on the center of the locally 4 closest beads.(Fig.1b).

A statistical parameter based on the Voronoi partition reveals successive densification regimes during the crystallization. An analysis based on the densest simplices reveals the presence of polytetrahedral clusters and characterizes their topology by counting the ring structures. We show that rings containing 5 tetrahedra are prominent features whose evolution shed light on the densification regimes.

EXPERIMENTAL SETUP

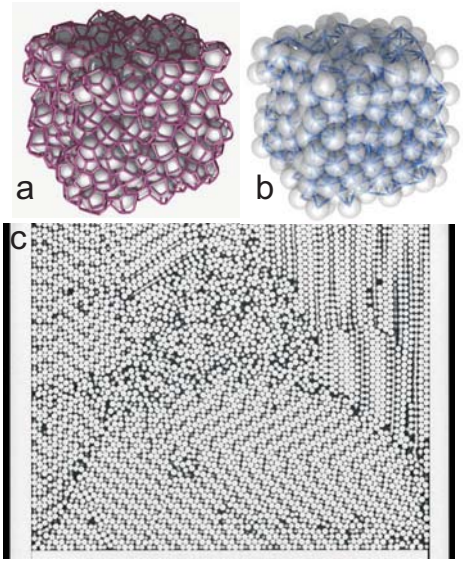

FIGURE 1. The Voronoi (a) and the Delaunay (b) partitions associated to some local configuration of beads extracted from the global packing.c) Radiograph of a partially crystallised packing obtained in a cylindrical container. It contains more than 200000 beads (diameter=1mm).

Our experimental setup is adapted from vibrating technics extensively used to study the compaction of disordered packings [2]. The experiments are performed with 1mm diameter acrylic beads that have a polydispersity within 2.5%. A batch of roughly 200000 beads is poured into a cylindrical or a spherical container. Initially the beads packings are in a random loose configuration with a volume fraction ϕ ranging from 57% to 61%. The packing is then intensively shaken, up to its fluidisation point, and a massive compaction is observed. The resulting packing is denser than $\phi \geq 0.685$. Inside the packing, large clusters (4000 beads) showing almost perfect crystallinity ($\phi \geq 0.732$) are formed. The internal structure of these packings is then imaged by means of X-Ray Helical Computing Tomography. Figure.1c shows a 2D slice through the tomogram of a dense packing obtained in a cylindrical geometry. The heterogeneous structure of the packing is obvious with almost perfectly crystalline clusters coexisting with disordered domains. We have consistently obtained this kind of partially crystallised packings for our two different geometries. The following analysis was carried out on the global packings and on subsets containing 4000 spheres.

LOCAL VOLUME FLUCTUATIONS

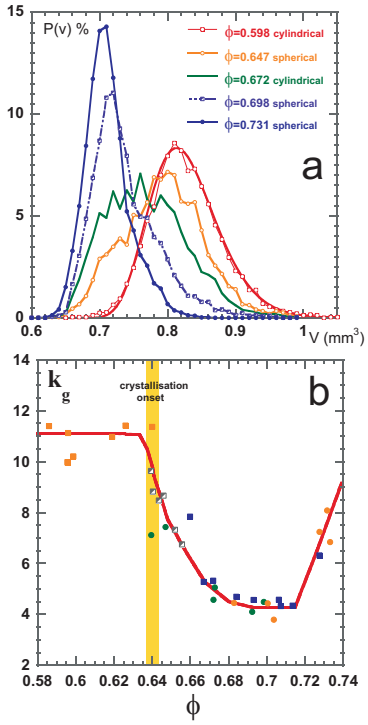

FIGURE 2. a) Probability distribution function (PDF) of the Voronoi cells volumes. b) $k_g = (\bar{V} - V_{min})^2/\sigma^2$ versus the volume fraction ϕ. k_g is computed from the volume fluctuations of the Voronoi partition [6]

To adress how local configurations get denser as the crystallisation proceeds, we use the Voronoi space partition (Fig.1a). The Voronoi partition allows to estimate the local volume fluctuations, i.e: measuring a probability density function (PDF) of the cells volume, its variance σ^2, mean value $\bar{V}$, its minimal bound V_{min}...

Figure 2a shows the probability distribution of the local Voronoi volume for a decreasing global volume fraction ϕ. When ϕ is below 0.64, the PDF for jammed packing is asymetric with an exponential tail and can be fitted by a gamma law [6]. For ϕ within [0.64,0.68] the PDF flattens and have a high level of fluctuations. As the

packing gets denser the PDF is more and more peaked around $V = 0.71mm^3$ which corresponds to crystalline configurations (i.e: a cubo-octahedra cell).

A quantitative charaterization of the local volume fluctuations is given by the parameter $kg = (\bar{V} - V_{min})^2/\sigma^2$ which was recently suggested as the granular material's equivalent of a "specific heat" [6]. This parameter reveals three successive structural transitions occurring in our packings at Φ =0.64, 0.68, 0.72 as shown in Fig.2b. Thus kg seems to be sensitive to the crystallisation onset occuring at $\Phi \approx 0.64$. Numerical simulations of perfectly monodisperse beads [6] have reported a monotonous drop of kg for $\phi > 0.64$. This drop was further analysed in terms of an entropy and considered as reminiscent of the Kauzmann paradox in supercool liquids. In our experiments, packing crystallisation turns out to be more varied than this monotonous scenario. The transitions observed at high density $\phi > 0.68$ might be connected to global transformations of the crystalline clusters [9].

POLYTETRAHEDRAL CLUSTERS

Definition and statistical description

The volume of a Voronoi cell is extremely correlated to the volume of its neighbours, it thus condemns any simple local description. To get insights into the structural changes occurring at the RCP ($\phi \approx 0.64$) and beyond, the packing will now be described in terms of its Delauney simplices (Fig1.b). The regular configuration of a simplex is the tetrahedron which represents the densest way to pack 4 monodisperse spheres together. In his seminal work, Bernal observed that clusters made of quasi-regular tetrahedra (*polytetrahedral* clusters) actually exist in random packings [5]. Recent numerical simulations [8] suggest that an increasing fraction of these clusters provides a densification mechanism for disordered packings. But this densification process has its limit and it saturates at the RCP density where the fraction of beads which are not involved in a polytetrahedral cluster is exhausted.[8] To compare our experimental results with these numerical simulations we first need to define two ingredients of this approach:

- what is a dense simplex (Bernal's quasi-regular tetrahedron) within the Delaunay partition?
- what is the aggregation mechanism producing clusters made of these tetrahedra?

A simplex is considered dense if the difference δ between its longest edge l and the average diameter d of the beads that compose the simplex is smaller than 25%.[8] In the following a dense simplex ($\delta = l - d \leq 0.25$) will be called a tetrahedron.

In an assembly of tetrahedra those who share a face should show a greater mechanical stability than tetrahedra connected via an edge or a vertex. Given this local stability criterion, we consider *polytetrahedral* aggregates as clusters built from three or more face-adjacent quasi perfect tetrahedra [5, 8]. Such clusters can't be part of any periodic crystalline lattice.[7]

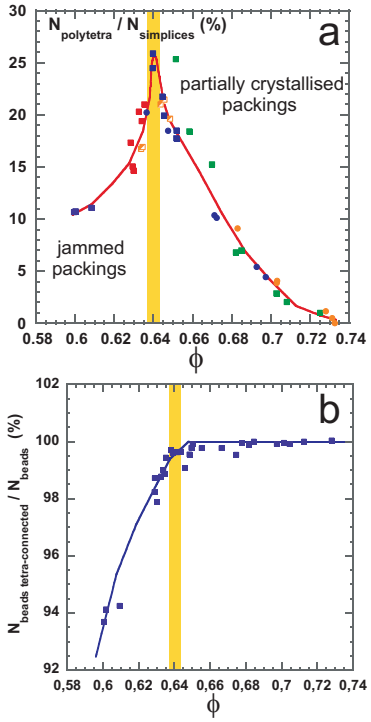

FIGURE 3. a) fraction of tetrahedra that are face adjacent and are involved in aggregates (*polytetrahedral clusters*) containing more than 3 components. b) fraction of beads which are part of at least one dense tetrahedron.

Figure 3 shows the main characteristics of these polytetrahedral clusters in our experimental packings for $\phi \approx 0.59$ up to $\phi \approx 0.73$. The fraction of polytetrahedral clusters has a sharp maximum around $\phi \approx 0.64$ (Fig.3a). At this peak, almost all the tetrahedra present in the packing are involved in a frustrated cluster [8]. Above $\phi \approx 0.64$, polytetrahedral clusters fade away progressively. At $\phi \approx 0.64$, all the beads are 'in contact' with a dense tetrahedron and are thus involved in a polytetrahedral cluster (Fig.3b).

Our experiments thus confirm the saturation phenomenon reported in [8]. The selection of distorted tetrahedra via the criterion δ confirms the organisation of disordered packings into polytetrahedral clusters [5] and reveals that a significant amount of these structures survives beyond the RCP.

A key topological descriptor: 5-rings

We will now elaborate on one key topological feature of the polytetrahedral aggregates and its evolution during the densification from random structures to quasi perfect crystal. In dense packings, polytetrahedral clusters have a natural propensity to form ring structures. Most of these rings contains 5 tetrahedra (5-rings) connected via complex linear branches (Fig.4a, [5, 7, 8]). A 5-ring pattern is one of the densest local configuration accessible with monodisperse spheres [7]. We have used a network analyser to describe the topology of the polytetrahedral aggregates. Our aim was to quantify the fraction and the size distribution of ring patterns inside a packing and their evolution all the way to the perfect crystal.

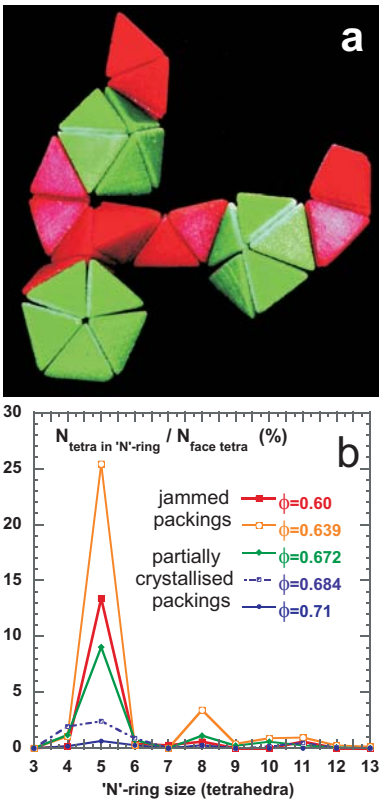

FIGURE 4. a) View of a polytetrahedral cluster made out of tetrahedra dices. Loops composed of 5 face adjacent tetrahedra (5-ring structure, in green) are connected via linear branches of tetrahedra (in red). b) Distribution of the size (in tetrahedra) of the rings patterns of the polytetrahedral clusters versus the volume fraction ϕ. The distribution is normalized by the number of face adjacent tetrahedra $N_{facetetra}$.

Figure 4.b depicts the evolution versus ϕ of the rings size distribution normalised by the number of face adjacent tetrahedra. Below the RCP limit, a packing gets denser by forming an increasing fraction of rings which are mainly 5-rings (Fig4.b). The fraction of 5 rings is sharply peaked at the RCP bound. While this compaction mechanism saturates around the RCP density, 5-rings patterns still account for almost 80% of the tetrahedra involved into a ring structure up to $\phi \approx 68\%$ (Fig4.b). Above the RCP limit, 5-rings are disappearing, and for $\phi \geq 68\%$ they have almost vanished (Fig4.b). It suggests that beyond $\phi \geq 68\%$ 5-rings are geometrically frustrated patterns that cannot be accomodated anymore into the growing crystalline clusters [9].

CONCLUSION

As a packing cristallises, it undergoes successive structural transitions ($\phi \approx 0.64 - 0.68 - 0.72$) revealed by the statistics of the local volume fluctuations. The consideration of dense tetrahedral configurations of beads inside a packing enlightens some of these morphological changes. It was confirmed that the fraction of polytetrahedral clusters is sharply peaked at the RCP limit. At this point, there are no more free beads to be incorporated into the polytetrahedral aggregates and crystallisation begins. A key topological feature of these aggregates are rings composed of 5 tetrahedra. The evolution of these 5-ring patterns gives a clearer picture of the crystallisation induced grains rearrangements. On the one hand, the RCP bound is a fully frustrated limit showing a maximum of highly dense 5-rings configurations. On the other, the transition observed at $\phi \approx 0.68$ corresponds to the 5-rings disappearance.

These findings should help to understand some of the mechanical properties of partially crystallised packings [10]. The propensity of the tetrahedra to coalesce via their faces might be interpreted as the existence of a directional entropic force [11]. It gives hope for the elaboration of a relevant statistical framework for granular crystallisation.

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