Crystallization of Confined Non-Brownian Spheres by Vibrational Annealing

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We introduce an experimental method to crystallize ensembles of non-Brownian spheres confined in narrow containers. The method is based on programed vibrations and a cooling procedure (annealing). Starting with a granular gas, the system slowly relaxes into a solid ordered structure: Body-centered-tetragonal and face-centered-cubic single crystals are obtained depending on the dimensions of the capillaries. Dry and lubricated beads behave differently, indicating that a sticking coefficient between the particles is important in the dynamics of the crystallization.

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Many studies, in different fields of science and technology, have been inspired by the problem of granular compaction [1]. Among the countless examples found in the literature related to this problem, we can mention the classic ball-bearing compaction model proposed by J. D. Bernal in 1959 to explain the structure of liquids [2], or more recently, the dynamics of a granulate made of spherical beads under shear devised as a useful analogy to understand the still elusive glass phase of matter [3].

When a cylindrical container is filled with spherical beads of the same size, the volume density of the unperturbed granulate will lie in the range of 0.56–0.58. Such a system is called, after G. D. Scott [4], the random loose packing. However, upon imposing vertical taps or a periodic vibration to this container, a logarithmic relaxation towards a denser state occurs [5]. The density of such state fluctuates around the value of 0.64, corresponding to a random close packing. A general consensus in the literature is that the observed logarithmic relaxation of the granulate, whose density never reaches the permissible value of 0.74 corresponding to an hexagonal-close-packing structure, is due to a frustrated dynamics resulting from excluded volume effects [6].

The compaction of an ensemble of spherical beads confined not in a cylindrical container but in a rectangular box, was first studied in 1997 by Pouliquen *et al.* [7]. The authors vibrated the system horizontally while beads were added to the container. This procedure, in analogy to its atomic counterpart, could be taken as an epitaxial technique conducted in an open system where particles are slowly incorporated. With this method, Pouliquen *et al.* obtained a density greater than 0.64 but less than 0.68. They studied the dynamics of the granular systems under different excitation conditions and filling rates and found that low rates are necessary to get a high volume fraction. More recently, a similar epitaxial-like method for the formation of hexagonal-close-packing (hcp) granular crystals in triangular containers was reported by our group [8]. The growth of the hcp stacking occurs also layer by layer, where relaxation in each one is governed by the inelastic collisions of the beads added to the container. Our epitaxial method can be also used in rectangular cells: as an example, an fcc crystal grown by this technique is shown in Fig. 1.

Despite the previous efforts in compaction studies, an important question remains unsolved: why granular ensembles like the one shown in Fig. 1 cannot be stacked in a closed system; that is to say, when all the beads are already in the container? Even if the geometry of the container is commensurable with the expected final arrangement, once the crystal in Fig. 1 is melted by strong vibrations, we cannot recover it again. Regardless the time given for the relaxation; under vertical, horizontal, continuous or tapped vibrations, jamming, with a random close packing density, is the final result. The aim of this Letter is to introduce a vibrational annealing method to overcome granular jamming in confined closed systems.

Confinement has been thoroughly investigated since the pioneering results of Jackson and McKenna [9], who found that the melting point of organic molecules confined in nanoporous materials is a function of pore size. Capillary condensation, wetting, glass, and freezing/melting transitions shifts, are other examples of molecular phenomena driven by the proximity and influence of walls in porous materials or small cavities [10]. Moreover, the freezing

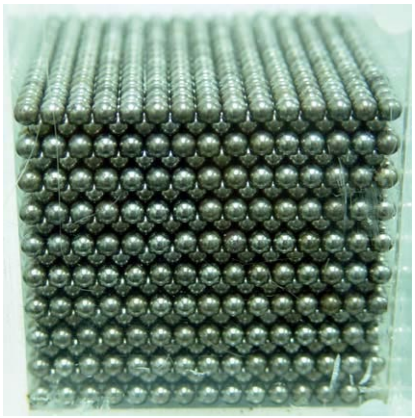

FIG. 1 (color online). An fcc stacking grown by epitaxy. The diameter of the ball bearings is 4 mm.

transition has been studied when hard spheres are confined within pores [11], as well as the dynamics of the crystallization and glass transition when they are in cavities with different surface roughness [12]. Vibrational annealing, on the other hand, is a method already introduced to remove local configurations during granular compaction experiments [13].

The experimental setup consists of a vertical shaking system driven by a function generator (HP-33120A), an amplifier, and a controlling computer. Plexiglas cells of triangular and rectangular bases (the dimensions of the cells we used range from 2.54 to 12 cm per side and 20 cm in height) are used in the experiments.

The first container we used was a rectangular cell of 25.4 mm per side and the beads were ball bearings with diameter 3.17 mm. In such a ''capillary'' [14], it is easy to grow, with the epitaxial technique above mentioned [8], a defect-free fcc stacking with (110) planes parallel to the walls [see Fig. 2(a)]. By its own right, the epitaxial growth of this crystal is an interesting granular phenomenon whose dynamics has been discussed before [8]. Our interest here is to start with a random loose packing (the configuration right after pouring the beads inside the capillary) or melting the structure shown in Fig. 2(a)], to obtain, by relaxation, the same crystal. Since the main strength of annealing is to remove local configurations that poison structural order, we expect that in our conditions (granular ensembles confined in narrow containers where the number of local random configurations is low) annealing can be successful to do the job.

We used a square vibration with amplitude $A(t)$ and linear frequency $\nu(t)$ (see Fig. 3). This vibration was needed in order to give more energy to the granulate, but a sinusoidal excitation works as well if enough power is available. During the first minutes, the vibration is strong enough to gasify the entire granulate. Thereafter, when the vibrations go down in amplitude, the granulate transits from a fluidized phase to a solid phase. A crystal with no defects is obtained at the end of the cooling process. To our surprise, however, this is not the fcc crystal grown by epitaxy, but a body-centered-tetragonal (bct), see Fig. 2(b). A bct structure is metastable, the stable fcc being a special case of it (when the ratio c/a is $\sqrt{2}$, the bct gives rise to the fcc). The first two planes of the bct crystal have 81 beads, compared to the more gravitationally stable fcc structure (113 beads).

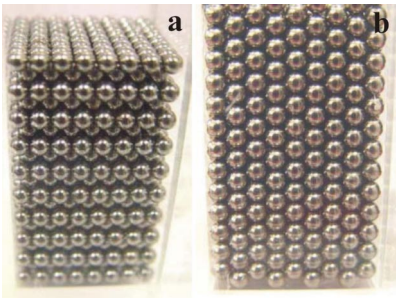

FIG. 2 (color online). A monodisperse stacking in a rectangular confinement (25.4 mm $\times$ 25.4 mm). The particles are 3.17 mm diameter ball bearings. (a) Face-centered-cubic structure grown by epitaxy. The plane parallel to the page is the (110) plane. In the first (third, fifth, etc.) plane there are exactly 64 beads, while in the second (fourth, sixth, etc.) 49. (b) Body-center-tetragonal structure obtained by annealing.

The second container is the one used to grow epitaxially the fcc shown in Fig. 1 (60 mm per side), and the ball bearings have a diameter of 4 mm. Such structure (Fig. 1) has in the first (third, fifth, etc.) plane 225 beads, while in the second (fourth, sixth, etc.) 196. Melting this crystal by large-amplitude square vibrations and going through a cooling program (annealing), we end up with fractured structures. At first sight, it appears that annealing is not able to promote global ordering. We have tried different cooling rates and always obtained the same result. However, we accidentally discovered that using lubricated ball bearings (for instance, as they are originally shipped by the fabricant) crystallization is feasible. Dry ball bearings that do not self-organize by annealing, amazingly do when a drop of oil is added to the system [see Fig. 4(b)]. We speculate that the small amount of oil covering the surface of the ball bearings introduces a sticking coefficient between the beads. We tried to induce granular crystallization using, instead of oil, a dry lubricant (graphite powder or stain-steel microspheres). We never get crystallization and therefore, concluded that friction or the restitution coefficient between the beads are not crucial parameters.

The structure found by annealing [Fig. 4(b)] is also an fcc, but it has a different orientation compared to the one grown by epitaxy (it is rotated 45 degrees; see the top views in Figs. 4(a) and 4(d)]. The number of beads in the first two planes of the epitaxially grown fcc structure [Fig. 4(a)] is 421 while this number is 442 for the fcc crystal shown in Fig. 4(b). To understand why two fcc structures have different volume fractions, bear in mind that these are confined and, therefore, finite-size effects affect their densities.

Other combinations (different aspect ratios and beads) can be used as long as commensurability within the containers is satisfied. For instance, an ensemble of glass beads

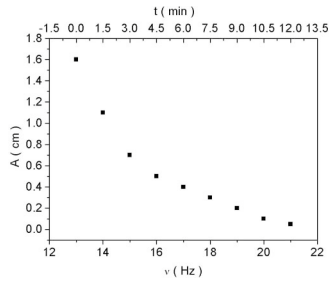

FIG. 3. Cooling rate for the annealing process. Amplitude and linear frequency of the square vibration as a function of time.

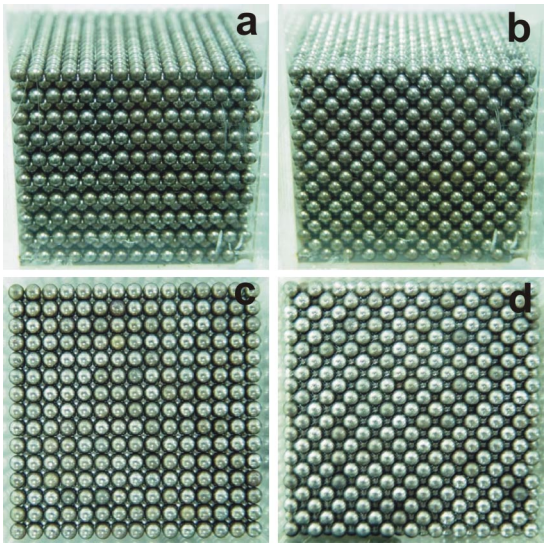

FIG. 4 (color online). fcc structures obtained by epitaxy and annealing: (a) epitaxy, (b) annealing. Parallel to the page are the (110) and the (100) planes of both fcc structures, respectively. The rotation of the crystal is clearly observed by looking at the top views (c) and (d).

or a mixture of glass and metal 4 mm diameter beads can be annealed into bct crystals (Fig. 5) or 1.6 mm ball bearings give rise to fcc crystals [Fig. 6(a)]. An important experimental finding is that granular convection imposes a size limit to our crystallization method. For example, ball bearings of 800 μm in diameter cannot be annealed into a crystal due to the persistence of convection (see the random final structure in Fig. 7).

We now investigated the crystallization of ball bearings in a much larger box. We used different periodic excitations (sinusoidal, square, triangular), distinct cooling rates, and several types of lubrication; the obtained packing never relaxes to a single crystal. We believe that the tendency of the beads to wet the bottom of the container and form orange-pile arrangements (with hexagonal (111) planes parallel to the base) inhibits perfect order. Although gravitationally stable, this hexagonal stacking is not fully

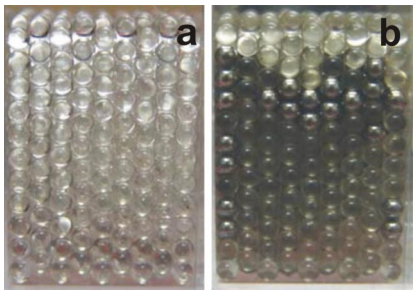

FIG. 5 (color online). (a) bct structure obtained by annealing with glass beads of 4 mm in a confinement of (32 mm $\times$ 32 mm). The plane parallel to the page is the (110) plane. (b) bct structure obtained by annealing with a mixture of glass beads and ball bearings of 4 mm in the same confinement.

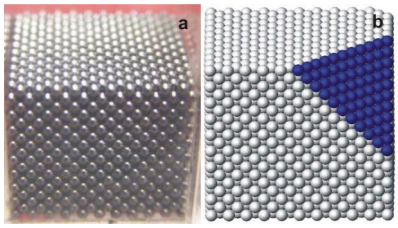

FIG. 6 (color online). (a) fcc structure obtained by annealing using ball bearings of d = 1.6 mm in a square confinement of 24 mm. (b) The same structure drawn by computer. We diagonally cut this structure to observe the hexagonal (111) planes.

commensurable with the square cross section of the confinement and defects appear. Nevertheless, annealing helps to diminish randomness, as can be clearly observed in Fig. 8.

It is interesting to observe the evolution of the hexagonal planes in the annealed structures as we change the dimensions of the confinement: in the bct crystals the hexagonal planes are vertical; in the fcc structure, diagonal; and in the structure annealed inside the largest container, horizontal.

In very narrow cells, walls are so close each other that sheared beads are forced to pack hexagonally in planes parallel to these walls [see Fig. 2(b)], forming, consequently, bct structures. The only condition for these structures to form is that the hexagonal planes fit the area of the walls. We see in Fig. 2(b) that this happens if there is an integer number of conventional cells within them. As the confinement is enlarged, wall shearing is not sufficiently strong to self-organize the beads into bct configurations. We believe gravity drives the rotation of the hexagonal planes until an fcc crystal, with sequence $ABCABC\ldots$, fit diagonally inside the container [see Fig. 6(b)]. Finally, the hexagonal planes collapse to the bottom of the cell when the distance between the walls is further increased; but since an $ABCABC\ldots$ sequence cannot fill the cross section

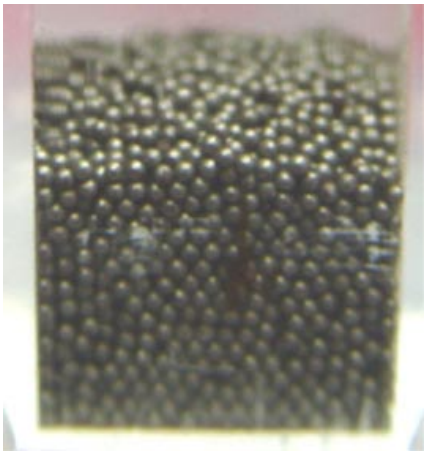

FIG. 7 (color online). 0.8 mm diameter ball bearings in a rectangular confinement of 12 mm. Because of granular convection, annealing fails to crystallize the system.

FIG. 8 (color online). fcc structure obtained by annealing with a large fracture. The plane parallel to the page is the (111) plane. The dimensions of the container are 120 mm × 120 mm and the diameter of the beads is 4 mm.

of the container, no single crystal can be formed (see Fig. 8).

About the crystallization of particles confined in triangular cells, is important to remark that annealing fails to form hcp structures like the one shown in Fig. 9. The reason is the following: due to the fact that the hexagonal (111) horizontal planes are commensurable with the triangular cross section of the container, the beads tend to pack following an orange-pile $ABCABC\ldots$ fashion. However, this fcc structure cannot completely fill the cell and thus, disorder appears.

In conclusion, in rectangular narrow containers, hard spheres can overcome, by annealing, the vitrified phase observed in large granular systems and relax into single bct or fcc crystals. In larger boxes, gravity forces the system to relax in such a way that hexagonal planes wet the base of the container; annealing helps to avoid a jammed granular state, but single crystals cannot be obtained. The rotation of the hexagonal planes is clearly promoted by the interplay among wall shearing, confinement, and gravity. Our results are important in several contexts: for making granular structures to be used as photonic and phononic crystals [15,16], in model systems to study stress propagation [17], or as a granular compaction technique in industrial processes. Future work aims to simulate, by molecular dynamics, the annealing of confined hard-sphere ensembles. We would like to computationally produce granular crystals as observed in the laboratory, to learn about the physics of the crystallization as we systematically change the important parameters of the system.

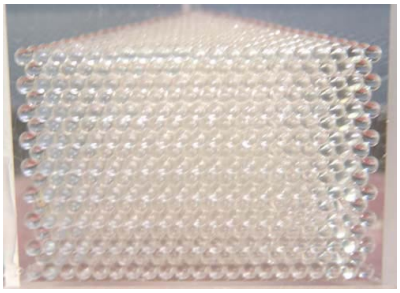

FIG. 9 (color online). A hcp ($ABAB\ldots$) structure of glass beads grown epitaxially [8].

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[1] T. Aste and D. Weaire, in *The Pursuit of Perfect Packing* (Institute of Physics Publishing, Bristol, 2000).
[2] J. D. Bernal, Nature (London) **183**, 141 (1959).
[3] G. D'Anna and G. Gremaud, Nature (London) **413**, 407 (2001).
[4] G. D. Scott, Nature (London) **188**, 908 (1960).
[5] J. B. Knight *et al.*, Phys. Rev. E **51**, 3957 (1995).
[6] D. A. Head, Phys. Rev. E **62**, 2439 (2000).
[7] O. Pouliquen, M. Nicolas, and P. D. Weidman, Phys. Rev. Lett. **79**, 3640 (1997).
[8] Y. Nahmad-Molinari and J. C. Ruiz-Suarez, Phys. Rev. Lett. **89**, 264302 (2002).
[9] C. L. Jackson and G. B. McKenna, J. Chem. Phys. **93**, 9002 (1990).
[10] L. D. Gelb, K. E. Gubbins, R. Radhakrishnan, and M. Sliwinska-Bartkowiak, Rep. Prog. Phys. **62**, 1573 (1999).
[11] Kegel and W. K. Kegel, J. Chem. Phys. **115**, 6538 (2001).
[12] Z. T. Nemeth and H. Lowen, Phys. Rev. E **59**, 6824 (1999).
[13] E. R. Nowak *et al.*, Phys. Rev. E **57**, 1971 (1998).
[14] Molecular or colloidal systems confined in capillaries have the important feature of a small aspect ratio (i.e., the diameter of the capillary is only few times the diameter of the particle). The granular systems studied here also have small aspect ratios.
[15] S. X. Yang *et al.*, Phys. Rev. Lett. **88**, 104301 (2002).
[16] Z. Y. Liu *et al.*, Phys. Rev. B **62**, 2446 (2000).
[17] D. L. Blair *et al.*, Phys. Rev. E **63**, 041304 (2001).