Epitaxial Growth of Granular Single Crystals

Y. Nahmad-Molinari and J. C. Ruiz-Suárez*

Departamento de Física Aplicada, CINVESTAV-IPN, Unidad Mérida, A.P. 73 "Cordemex," Mérida, Yucatán 97310, México

(Received 30 August 2002; published 11 December 2002)

Compaction from a random-loose-packed to a random-close-packed phase is observed when monodisperse granular beds are shaken, but beyond this packing, the system freezes up in a jammed structure. Here we report a technique to grow large hard-sphere granular crystals, with perfect stacking and no defects by means of a "gas phase" epitaxial procedure. We study the growth mechanism and provide evidence that the observed granular crystallization is driven by gravity and energy dissipation.

DOI: 10.1103/PhysRevLett.89.264302 PACS numbers: 45.50.–j, 45.70.Cc

Hard spheres, both in computer simulations and in the laboratory, have been for many years useful model entities to advance the understanding of fundamental problems in statistical mechanics, such as nucleation, crystallization, and the so-called glass transition. In the last decade the study of the dynamics of hard-sphere colloidal assemblies has produced a significant number of reports in the scientific literature (see [1] for a review). One of the main conclusions of this intensive research is that the phase diagram of colloidal hard spheres is athermal and governed completely by entropy. In addition, techniques to grow large colloidal crystals have emerged: among them an epitaxial technique based on the slow sedimentation of hard spheres onto a patterned substrate [2] and a temperature gradient driven method [3]. These two techniques will, very likely, contribute soon to technological applications in the incipient industry of colloidal crystals [4].

Going from hard-sphere colloidal suspensions to granular beds, a very different scenario appears: while in hard-sphere colloidal systems temperature does not play a role, and gravity precludes any crystallization beyond a volume fraction of 0.59 [5]; in granular packings both gravity and "granular temperature" are essential variables to seek for structural order. Granular structures have important applications as photonic and phononic crystals [6–9], in model systems to study stress propagation [10,11], in the study of lattice dynamics [12], among others. Nevertheless, attempts to avoid the frustrated relaxation of granular packings toward defect-free crystal structures have failed [13,14]. Until now, the closest packing achievable by vibration or shaking is around 0.68 of volume fraction, still far from the ideal 0.74 corresponding to a perfect single hexagonal-close-packed (hcp) structure [15]. A purely mechanical method has been reported to circumvent this problem and make large hcp granular crystals [10]. Such a method consists in vacuum holding a complete hexagonal layer of beads on a perforated plate and the subsequent release of one layer after the other until a perfect structure is formed. Upon construction, a small number of defects are removed by hand before depositing the next layer.

The aim of this Letter is to report a technique to grow large hard-sphere granular crystals with perfect stacking and no defects. The technique is based on a gas phase epitaxial procedure. We provide evidence that granular crystallization is driven by an interplay of gravity and energy dissipation.

Our experimental setup consists of a Plexiglas cell of an equilateral triangular base in which an exact number of particles fit in the first layer (the dimensions of the cells we used range from 5 to 15 cm per side and 20 cm of height). The cell is mounted on top of a vertical shaking system with an accelerometer attached to it. A particle feeder drops particles, one at a time, into the cell, at a given and controlled frequency. We used steel ball bearings of 3.175 mm in diameter. Dropping the balls at slow rates while vertically shaking the cell at a starting acceleration a just above g ($a/g = 1.09$) leads to the formation of a seed or an inelastic collapselike state (a cluster of motionless particles in constant contact [16]).

The term "inelastic collapse" refers to the state in which a group of particles undergoes an infinite number of collisions in a finite period of time. As a result, this group of particles comes into contact without any attractive forces between them. The main condition to have an inelastic collapse is that the energy dissipation rate should be large enough to promote self-stabilizing clusters [17]. Normally, a granular system of hard spheres will show inelastic collapse dynamics if the restitution coefficient between particles is less than unity. The restitution coefficient of the ball bearings has been reported to be about 0.90 [18].

Convergent velocity fluctuations, in the granular gaslike phase [19] within the cell, increase the density of a region, which then acts as a condensation nucleus. Clearly, the walls favor the appearance of these nuclei due to the lower restitution coefficients. The particles fed into the cell join one of the two coexisting phases, the collapse or the gas, until the density is high enough that the entire first layer becomes hexagonally close packed

underneath a pressing gas bouncing on top. Upon addition of further particles, the gas increases its density until eventually the embryos of a new crystalline phase start to appear. These embryos or aggregates are hexagonally packed due to the template beneath them, but they can grow in positions forming either islands type B or C (in the standard description of close-packed polytypes). When these two growing nuclei meet, a grain boundary may be formed which in turn starts the growth of a polycrystalline solid. In order to avoid the formation of such a structure, it is enough to have a slow rate of ball feeding, allowing the crystals congruent with the wall boundaries sufficient time to devour (coarsening) the crystals grown in the interior.

We note that the walls in our triangular cells act not only as condensation nuclei, but globally determine the perfect self-assembled hexagonal packing. If the confinement is not triangular nor commensurate with the hcp crystal structure, defects or grain boundaries would propagate from walls to the bulk of the solid. We believe that no conformal triangular confinement might be the origin of failed attempts reported in the literature to get 0.74 of volume fraction in granular stackings [15].

The vibrational energy supplied to the system must be sufficient for the gas particles to travel (and explore) at least two diameters before a new particle is added to the cell, allowing the coarsening process to correct the mismatches that could appear (in the limit of low feeding rate the crystal growth still takes place properly but is very slow; however, if the feeding rate is large, islands of any type can be buried in the granular solid and coarsening cannot correct mismatches). After the particles are supplied to the cell, they start exploring the free surface in a random walk until they find a potential energy well and can lose most of their kinetic energy faster than they receive it, nesting there and increasing the size of the crystal. To be able to deliver the kinetic energy they receive, the probability of collisions per unit time must be high; hence a good nesting place has the maximum number of nearest neighbors.

Following the above procedure, which can be seen as the granular analog to the epitaxial chemical vapor deposition method used for growing atomic crystals, we can grow defect-free hcp structures. In Fig. 1 we show two single crystals grown by our method, one with 8 000 particles and the other with 13 000. The numbers of particles in the first layer of these crystals are 120 and 300, respectively. It is important to mention that the vibrational energy supplied to the granular bed in the cell must increase continuously while the crystal is forming. The reason is simple to understand; the total energy provided to the system is transformed into kinetic energy of the beads already in crystal positions, heat and kinetic energy of the beads in the gas on top. Since the particles in the gas need to explore randomly the template underneath, they must have a constant reservoir of kinetic energy. Thus,

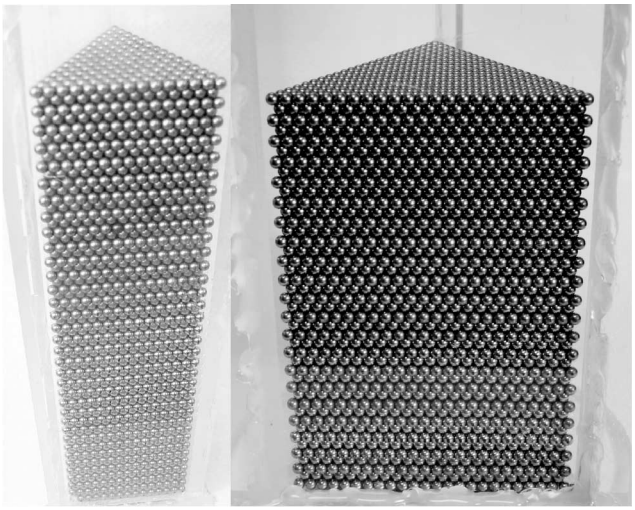

FIG. 1. Single hcp granular crystals grown by the epitaxial method. Left: Crystal with 5 cm side and 18 cm height, containing approximately 8000 steel ball bearings. The crystal was grown in about 2 h. Right: Crystal with 8 cm side and 11.5 cm height, containing approximately 13 000 steel ball bearings. The crystal was grown in about 3 h.

due to the fact that vibrations or phonons in the crystal already formed act as energy sinks, the vibrational energy supplied must increase at the same rate as the crystal is growing. There are two ways to increment the vibrational energy supplied to the system, increasing the amplitude A or the frequency of the vibrations. In our experiments, we maintain the frequency constant and increase only the amplitude.

We point out that the self-assembled granular structures grown by our method are hcp and not fcc typical of hard spheres. This is due to the fact that the fcc structure in a confinement like ours is not gravitationally stable. In other words, self-organization cannot lead to an $ABCABC\ldots$ structure. Indeed, once layers A and B are formed, C islands growing above them leave vacancies at the corners of the cell able to allocate type A particles. This implies that the third layer of the stacking cannot be purely C. Furthermore, A sites close to the walls on the fourth layer are not gravitationally stable. Particles falling into these sites would produce stresses against C-like particles. On the other hand, A islands on top of a B layer, are stable and congruent with the wall boundaries, leading to the hcp structure.

In order to quantify the dynamics of the crystallization process, we study the granular aggregation of a fraction of a monolayer (600 beads) on top of a complete layer formed by 1176 beads. By using appropriate diffuse illumination from above, we took snapshots every 15 s (see Fig. 2 for some examples). From these snapshots and using imaging software (IMAGE PRO PLUS), we obtained the center of each particle in the ensemble. In Fig. 2 each image in the bottom row is the Fourier transform of the

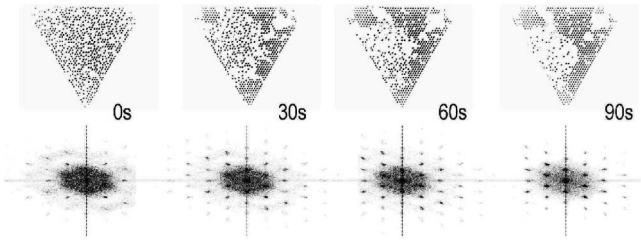

FIG. 2. Nucleation snapshots of a granular layer (in a 15 cm side cell) and their corresponding Fourier transforms for 0, 30, 60, and 90 s. The number of particles (600) is fixed. They are first randomly positioned on top of a complete hcp layer.

snapshot above it. In Fig. 3 we show the pair distribution function (inset) and a plot of the first peak of this distribution as a function of time. Since the top layer we follow is in registry with the hexagonal template underneath, this main peak is a direct measure of the number of particle contacts: the higher the peak the larger the number of these contacts. The growing rate of the particle density within a cluster, must be proportional to the number of free particles available in the layer or in smaller clusters. This can be expressed by the differential equation $dN_c/dt = \beta(N_T - N_c)$, where N_c is the number of particles in a cluster, N_T the total number of particles in the layer, and β a constant (interpreted physically as the aggregation time constant). The solution of the above differential equation is $N_T(1 - e^{-\beta t})$ (normalized and plotted as a solid line in Fig. 3). The fit gives β equal to $0.023\ s^{-1}$. Such dynamics describes the migration of the particles from the gas (or smaller clusters) to the crystal; the particles explore a large number of potential energy wells and nest just in the wells where a maximum number of collisions per unit time takes place. In inelastic collapses [20], observed in simulations and experimentally in 2D, the particles form straight lines or hexagonal packings. A perfect crystalline structure maximizes the number of linear arrays of particles, which in turn maximizes the number of collisions.

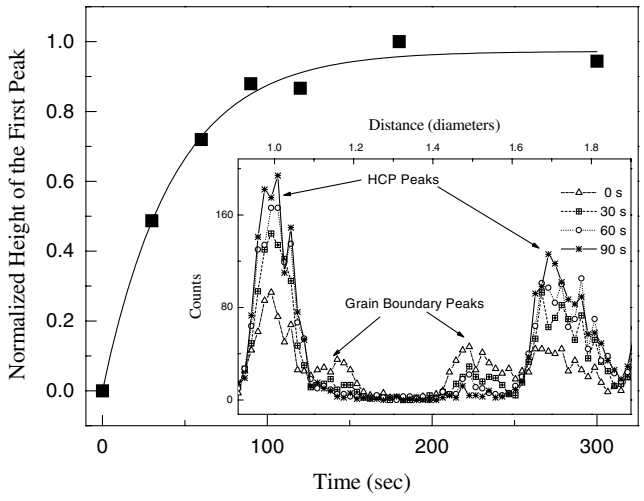

FIG. 3. Nucleation dynamics of the granular gas of Fig. 2. The evolution of the height of the first peak of the pair distribution function (inset) is shown as a function of time. For the sake of clarity we do not show in the inset all the pair distribution functions from which the experimental points (squares in the main figure) were obtained. The solid line represents an exponential saturation of the number of particle contacts. The "boundary peaks" in the inset show the dynamics of coarsening; at the same rate these peaks decrease the main peak increases.

Based on our experiments and the discussion above, we ought to distinguish between two different mechanisms: particles releasing their kinetic energy and relaxing into crystal positions and the underlaying mechanism behind the stability of the entire crystal. First, particles dropped into the cell during the crystal growth join, for a period of time, the granular gas. Each particle undergoes a chaotic trajectory (out of phase from the vibration system) with very large displacements. Thereafter, these particles arrive at a nucleus, relaxing through dissipation into crystal positions. In other words, this dissipation dynamics might be seen as the "microscopic" crystal growth mechanism. Second, once particles cool down into crystal positions, they are now in phase with the crystal vibration and the relative (to the crystal) displacements are very small. Thus, a reasonable hypothesis is that the physical mechanism to drive the observed crystallization is the minimization of both potential energy and energy dissipation. The first one is obvious, since the hcp crystal is the configuration with the minimum total potential energy (any other volume fraction will increase the height of the column and therefore the potential energy). The second, more subtle, implies that under vibration a disordered structure dissipates more energy.

In order to test the second part of the above hypothesis, we carried out the following experiment. A granular crystal grown by our technique is vibrated at a frequency of 97 Hz, and the input voltage amplitude of the sinusoidal signal supplied to the vibrating table is kept fixed. An accelerometer is attached to the base of the vibrating system. The voltage output of the accelerometer is proportional to its deformation, which in turn is proportional to the vibration amplitude. Its output gives a stable and reproducible sinusoidal voltage signal which is registered and recorded by an oscilloscope (HP 54600B). First, the crystal has 23 complete layers. Thereafter, the first two layers of the crystal are manually disordered (melted) and the signal from the accelerometer is again measured. This process continues until the entire crystal is completely melted. We show in Fig. 4 a plot of the accelerometer output vs the number of disordered layers in the crystal (the number of particles in the cell does not change). The exponential decrease of the amplitude clearly indicates that disorder (glass) presents greater vibrational impedance than order (crystal). In other words, a disordered

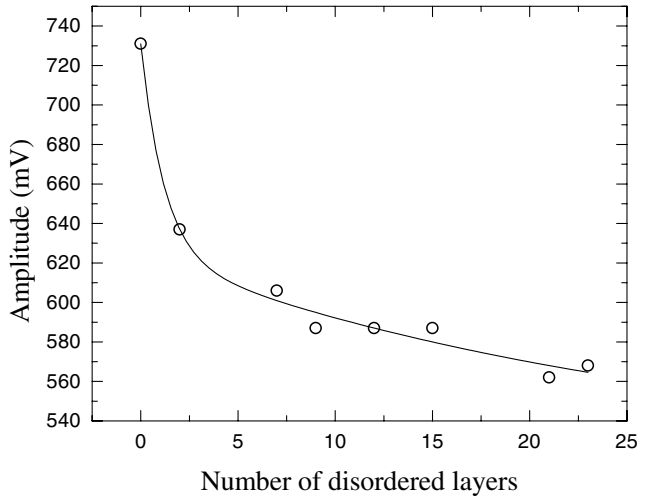

FIG. 4. Peak to peak vibrational amplitude vs number of complete disordered layers.

solid dissipates more energy than a crystal solid, so the principle of least dissipation of energy (or minimum production of entrophy) put forward by Prigogine [21] might be on the ground of granular crystallization.

We have described a new technique to grow perfect granular hcp crystals with the maximum volume fraction of 0.74. The phenomena of nucleation and coarsening, studied in colloidal suspensions of hard spheres, are also observed in our granular experiments. We also propose that the driving force for granular crystallization is based on gravity and the principle of least energy dissipation.

Y. N. M. acknowledges a support from CONACyT, Mexico. We thank D. Castillo-Fernandez for her help in the use of the IMAGE PRO PLUS software and E. Salazar-Neumann for the calculation of the pair distribution function. We also thank Cristian Moukarzel for his suggestion of measuring the system impedance. This work has been supported by CONACyT, Mexico, under Grant No. 36256E.

*Corresponding author.
Electronic address: cruiz@mda.cinvestav.mx

[1] T. Palberg, J. Phys. Condens. Matter **11**, R323 (1999).
[2] A. vanBlaaderen, R. Ruel, and P. Wiltzius, Nature (London) **385**, 321 (1997).
[3] Ch. Zhendong, W. B. Russel, and P. M. Chaikin, Nature (London) **401**, 893 (1999).
[4] J. D. Joannopoulos, P. R. Villeneuve, and S. H. Fan, Nature (London) **386**, 143 (1997).
[5] J. Zhu *et al.*, Nature (London) **387**, 883 (1997).
[6] W. Y. Zhang *et al.*, Phys. Rev. Lett. **84**, 2853 (2000).
[7] S. Yang *et al.*, Phys. Rev. Lett. **88**, 104301 (2002).
[8] Z. Y. Liu *et al.*, Science **289**, 1734 (2000).
[9] Z. Liu, C. T. Chan, and P. Sheng, Phys. Rev. B **65**, 165116 (2002).
[10] D. L. Blair, N. W. Mueggenburg, A. H. Marshall, H. M. Jaeger, and S. R. Nagel, Phys. Rev. E **63**, 041304 (2001).
[11] N. W. Mueggenburg, H. M. Jaeger, and S. R. Nagel, cond-mat/0111347.
[12] S. Alexander, Phys. Rep. **296**, 65 (1998).
[13] M. Nicodemi, A. Coniglio, and H. J. Herrmann, Phys. Rev. E **55**, 3962 (1997).
[14] J. B. Knight, C. G. Fandrich, C. N. Lau, H. M. Jaeger, and S. R. Nagel, Phys. Rev. E **51**, 3957 (1995).
[15] O. Pouliquen, M. Nicolas, and P. D. Weidman, Phys. Rev. Lett. **79**, 3640 (1997).
[16] M. Alam and C. M. Hrenya, Phys. Rev. E **63**, 061308 (2001).
[17] S. Luding and H. J. Herrmann, Chaos **9**, 673 (1999).
[18] J. S. Olafsen and J. S. Urbach, Phys. Rev. Lett. **81**, 4369 (1998).
[19] In this paper we use "granular gas" in order to distinguish the phase in which particles bounce and explore the region around the phase formed by particles already in equilibrium positions (granular solid). Note that we are not referring to the concept (still in debate) of a granular gas in a strongly vibrated column but to the granular gaslike phase concept previously used by Olafsen and Urbach (see Ref. [18]).
[20] I. Goldhirsch and G. Zanetti, Phys. Rev. Lett. **70**, 1619 (1993).
[21] B. H. Lavenda, *Thermodynamics of Irreversible Processes* (Dover, New York, 1978).