

## Nonequilibrium two-phase coexistence in a confined granular layer

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We report the observation of the homogenous nucleation of crystals in a dense layer of steel spheres confined between two horizontal plates vibrated vertically. Above a critical vibration amplitude, two-layer crystals with square symmetry were found to coexist in steady state with a surrounding granular liquid. By analogy to equilibrium hard-sphere systems, the phase behavior may be explained through entropy maximization. However, dramatic nonequilibrium effects are present, including a significant difference in the granular temperatures of the two phases.

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Statistical mechanics provides a powerful formalism for predicting the behavior of systems at or near equilibrium. Many natural phenomena, however, occur far from equilibrium, and extensions of the machinery of statistical mechanics to situations where significant energy flows are present would have a wide range of potential applications. Some success has been achieved in extending statistical mechanics to far-from-equilibrium situations. For example, techniques for calculating the relative probabilities of different configurations have been successfully developed for nonequilibrium steady states in a few restricted situations [1–3]. Also, effective temperatures based on the fluctuations in nonequilibrium steady states have been developed recently and, in some cases, have been found to equilibrate across different fluctuating quantities [4–10]. To generalize these initial successes to a broader spectrum of phenomena, and to develop insights into other facets of a statistical theory of far-from-equilibrium systems, new model systems for investigating nonequilibrium steady states must be developed and studied. Here we report our investigations of a simple, far-from-equilibrium granular system that shows that some mechanisms that operate in equilibrium appear to persist into situations far from equilibrium, whereas other basic tenets of equilibrium statistical mechanics must be substantially modified.

Granular materials are ubiquitous in nature and show a remarkable range of nonequilibrium behavior [11–13]. Dynamic steady states, achieved when energy input from an external source balances energy lost through inelastic collisions, provide an ideal testing ground for extensions of equilibrium statistical mechanics [4–6,10]. Here we report experimental measurements and computer simulations of the dynamics of spherical particles confined between two horizontal vibrating parallel plates. We observe a freezing transition from a homogeneous, disordered liquid to an ordered solid with square symmetry coexisting with a surrounding liquid. An essentially identical transition is observed in con-

finer hard-sphere colloidal suspensions in equilibrium [14–18], where it is driven by entropy maximization. The presence in both the granular and the colloidal system of a solid phase with the same unexpected symmetry which occurs under the same geometric constraints and at similar densities strongly suggests a common mechanism. Unlike the equilibrium system, however, we find that the coexisting phases have dramatically different granular temperatures, demonstrating that the “zeroth law” of thermodynamics is not followed by the granular temperature. Taken together, these results show that the driving mechanism behind an equilibrium phase transition may still operate far from equilibrium, but that a thermodynamic theory must account for the absence of equipartition in the kinetic energy of the particles.

The granular system is sketched in Fig. 1(a). Previous studies which used a similar geometry at lower shaking amplitude and lower density than what is presented here found a range of complex nonequilibrium phenomena including inelastic collapse [19,20], hexagonal ordering [19,21], non-Gaussian velocity distributions [19,20,22], and velocity correlations [23]. In our experiment, stainless-steel spheres of diameter  $\sigma=1.59$  mm were placed between a smooth anodized aluminum plate and an 11-mm-thick Plexiglas lid with an antistatic coating. A gap spacing of  $1.75\sigma$  between the plate and the lid was maintained by circular rings of aluminum and Mylar spacers. Using an electromagnetic shaker, the system was driven sinusoidally in the vertical direction with frequency  $\nu$  and amplitude  $A$ . The motion of the balls was imaged from above using a high-resolution camera (Pulnix TM1040). The results presented here were obtained for densities  $\rho=N/N_{\max}$  ranging from 0.8 to 0.9, where  $N$  is the number of balls in the system and  $N_{\max}=11\,377$  is the maximum number of balls that can fit in a single hexagonally close-packed layer at rest on the bottom plate. For modest vibration amplitude, the system appears liquidlike. As the vibration is increased, small independent unstable crystalline structures form. Increasing the vibration amplitude further causes the crystallites to become stable and eventually coalesce to form a single crystal which coexists with a surrounding granular liquid [see Fig. 1(b) and supplemental movie [24]]. The crystal consists of two layers, each with a square symmetry. The balls in the second layer are above the centers of the squares formed by the balls in the bottom layer. The

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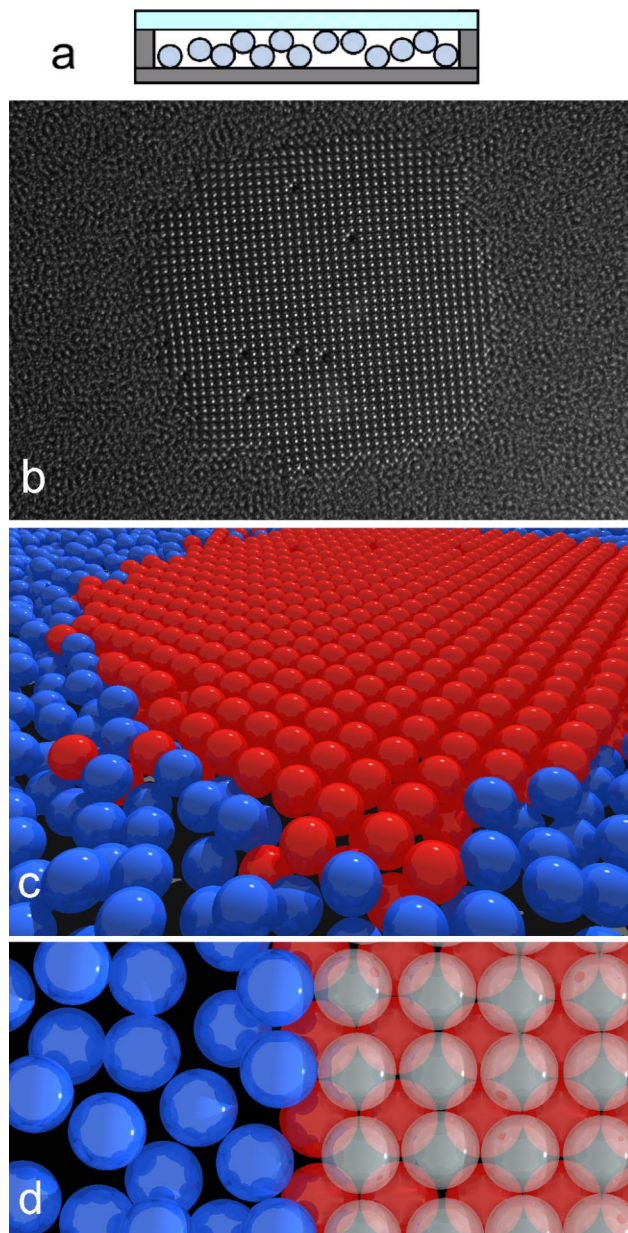


FIG. 1. Two-phase coexistence in steady state. (a) Side view of experimental setup. The system is shaken vertically and imaged from above. (b) Experiment: time-averaged image of ball positions. Only the top layer of the crystal is visible and there are several vacancies ( $A=0.085\sigma, \rho=0.9, \nu=80$  Hz, averaged over 1 s). See also supplemental movie [24]. (c, d) Simulation: 3D rendering of instantaneous ball positions. In (c), balls in the crystal are colored red, balls in the liquid are colored blue. In (d) a closeup of the crystal is shown with the top layer transparent. ( $A=0.13\sigma, \rho=0.89, \nu=60$  Hz, and 5000 balls.)

crystals are not densely packed and the balls constantly jitter around in the cage formed by their neighbors and the confining plates. Rearrangements continually occur at the interface, but the average size of the crystal does not change as long as the shaking amplitude and frequency are held constant.

In order to verify that the coexistence was not due to nonuniformities in the experimental apparatus, and to measure quantities not readily accessible in the experiment, we performed molecular-dynamics simulations using a model that has accurately reproduced many of the phenomena observed in a similar system [23,25]. Ball-ball, ball-plate, and ball-lid interactions are characterized by three forces: an elastic restoring force, a dissipative normal force which produces a velocity-independent coefficient of restitution, and a dissipative tangential friction. Periodic boundary conditions in the horizontal plane were used. The simulations reproduced the phase coexistence [Figs. 1(c) and 1(d)] and all of the general features of the observed phenomena, such as the existence of a critical threshold to nucleation and evaporation.

Perhaps the most surprising aspect of the transition we observe, the presence of a square symmetry instead of the hexagonal ordering naively expected for hard-sphere interactions, appears to be closely related to the phase behavior of suspensions of hard-sphere colloidal particles at similarly high densities in similar confining geometries [14–16]. For hard spheres the equilibrium configuration is determined by entropy maximization. For a range of gap spacings, including the spacing used in our system, two square layers pack more efficiently than two hexagonal layers, thereby maximizing the free volume available for each particle and therefore the entropy of the system [17,18]. The observation of a transition that closely matches an equilibrium, entropy driven phase transition suggests that a generalized free-energy functional might be found which describes the behavior of some driven granular materials.

Equilibrium two-phase coexistence requires that the two phases have equal temperatures, pressures (apart from surface-tension corrections), and chemical potentials. Recent work has focused on extending the concept of the chemical potential to nonequilibrium coexistence in which the first two conditions are satisfied [26,27]. To test whether these two conditions are met in this system, we measured the granular temperature  $T_g = \langle v_i^2 \rangle$ , where  $v_i$  is a horizontal component of the rapidly fluctuating velocity of a particle. In the experiment, particle displacements were measured using the particle imaging velocimetry technique described in Ref. [23]. Using the method described in Ref. [22], we verified that the temporal resolution was sufficient to accurately measure instantaneous velocities. In both the experiments and simulations, we investigated whether the granular temperature equilibrated to the same value in the two phases. As shown in Figs. 2(a) and 2(b),  $T_g$  is dramatically lower in the crystal than in the surrounding liquid, both in the experiments and in the simulations. The spontaneous separation into phases of different temperatures in a homogeneous system of identical particles is a striking effect that will have to be incorporated into models of nonequilibrium phase coexistence. It is somewhat reminiscent of “inelastic collapse” [19], but in that case the absence of any significant granular temperature in the solid phase arises from the bistability of the ball-plate dynamics at low vibration amplitudes [28,29]. The results described here are observed at high vibration amplitudes where there is continuous energy input from the plate into both coexisting phases. The pressures of the two

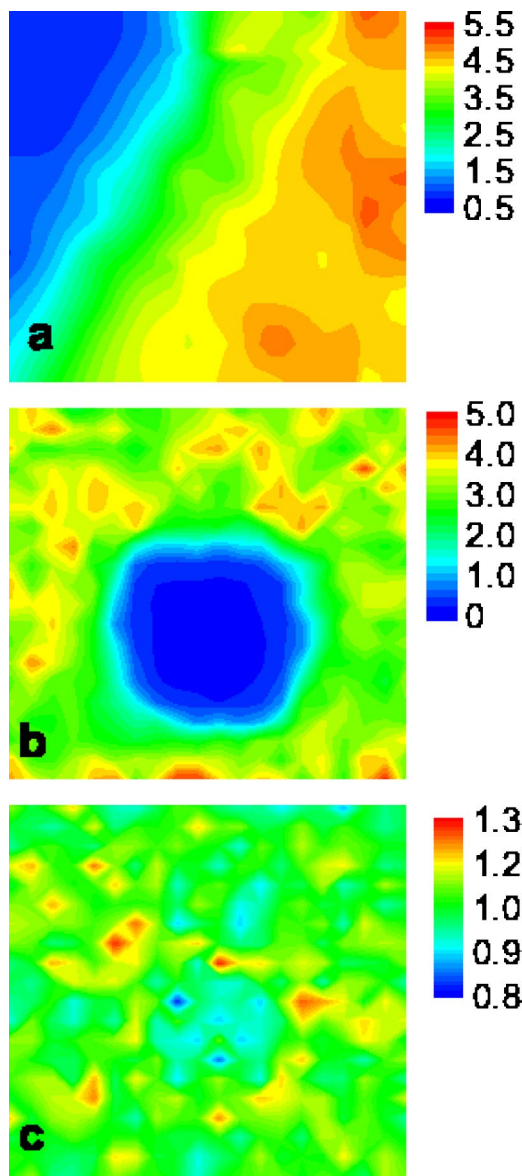


FIG. 2. Temperature and pressure fields. (a) Temperature field near the liquid-solid interface, measured in the experiment, averaged over about 40 s. The crystal is in the upper left. ( $\rho=0.85$ ,  $\nu=60$  Hz,  $A=0.154\sigma$ , displacements measured over 0.33 ms.) (b) Temperature field and (c) pressure field from the simulation shown in Fig. 1(c), averaged over 2.5 s. The crystal is in the center. The pressure was calculated using the virial expression, as described in Ref. [30].

phases calculated in the simulations have nearly the same value, but the pressure is slightly smaller in the solid phase [Fig. 2(c)].

To further study the properties of the phase coexistence, we investigated the nucleation of the crystalline phase. Starting with the vibration amplitude at a low value, we slowly increased the intensity of shaking and measured the amplitude at which the crystalline phase first nucleates. This procedure was repeated for several densities between  $\rho=0.8$  and 0.9, and for frequencies between  $\nu=45$  and 100 Hz. A typical curve of the frequency dependence is displayed in Fig. 3(a) for  $\rho=0.85$ . In addition to this “nucleation line,” we also

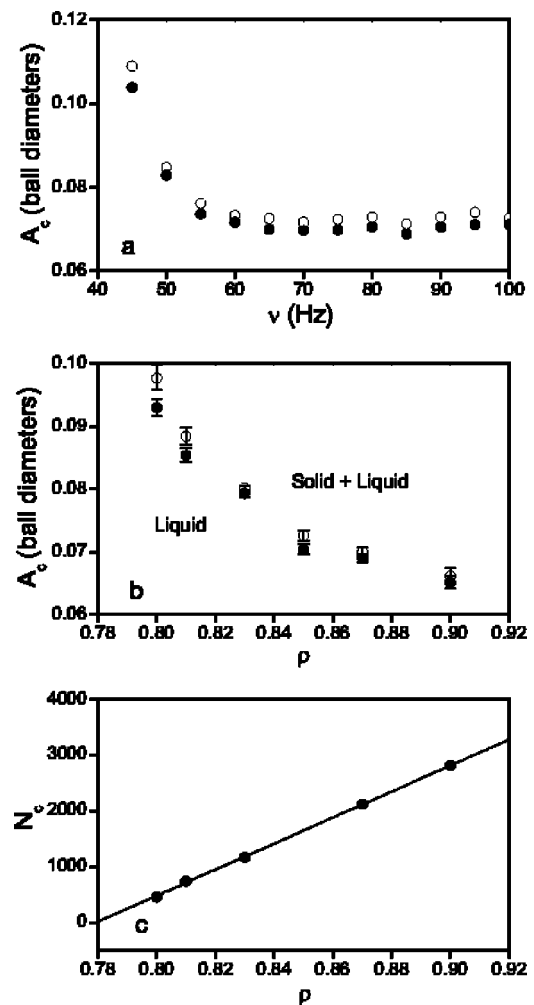


FIG. 3. (a) Frequency dependence of the critical amplitudes  $A_C$  for nucleation (open circles) and evaporation (black disks) at  $\rho=0.85$ . (b) High-frequency plateau value of  $A_C$  as a function of  $\rho$ . (c) Average number of balls of the crystal,  $N_C$ , as a function of  $\rho$  ( $\nu=60$  Hz,  $A=0.145\sigma$ ). Each point represents the average of 10 measurements well separated in time. The solid line is a linear fit to the points.

determined an “evaporation line” by slowly decreasing the amplitude until the crystal disappeared. For  $\nu$  greater than 60 Hz, we found that the critical amplitudes were roughly independent of frequency. This high-frequency behavior was found at all densities, but the cutoff frequency increased as the density increased. One possible explanation for a frequency-independent critical amplitude is that the vibration may effectively compress the layer. If the balls are moving slowly compared to the plate and lid, then they will be mostly confined between the maximum plate height and minimum lid height. This increase in the density of the system favors nucleation of the crystal. This frequency-independent behavior cannot persist to low frequencies, however, because the acceleration, which is proportional to  $\nu^2$ , must be significantly larger than that due to gravity for the balls to have enough kinetic energy to reach the second layer. We used the average value of the amplitude in the high-frequency plateau (60–100 Hz) to define a critical am-

plitude,  $A_C$ , and we constructed a “phase diagram” of  $A_C$  versus  $\rho$  [Fig. 3(b)].  $A_C$  varies from roughly  $0.06\sigma$  at  $\rho=0.9$  to  $0.1\sigma$  at  $\rho=0.8$ .

We measured the dependence of the crystal size on the number of particles in the system by analyzing the images to extract  $N_C$ , the number of spheres in the crystal [31]. As shown in Fig. 3(c),  $N_C$  varies linearly with  $\rho$  and extrapolates to zero at  $\rho=0.78$ . In steady-state coexistence, the edge of the crystal is “in equilibrium” with the surrounding liquid of density  $\rho_L$ . Assuming that the densities of the coexisting crystal and liquid are independent of the size of the crystal, the area  $A$  occupied by the crystal of density  $\rho_C$  should satisfy the relation  $A/A_T=(\rho-\rho_L)/(\rho_C-\rho_L)$ , where  $A_T$  is the total surface area of the plate, so that  $N_C\propto(\rho-\rho_L)$ . The value of  $\rho_L$  found by extrapolating to  $N_C=0$  agrees with direct measurements of the density of the granular liquid in the coexistence region.

No formalism exists for incorporating the entropy into a

predictive theory on nonequilibrium phase transitions, but our results indicate which parts of the equilibrium framework need modification. The large difference in the granular temperature of the coexisting phases demonstrates that the “zeroth law” of thermodynamics is not satisfied by the granular temperature. An effective temperature that does meet this requirement is probably a necessary ingredient of a quantitative theory of the phase coexistence. By comparing the system described here with the analogous and well-understood equilibrium system, new approaches for incorporating the effects of forcing and dissipation into a statistical mechanics of nonequilibrium phase transitions can be developed and tested.

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 [24] See EPAPS Document No. E-PLIEEE8-70-R15410 for a supplemental movie of Fig. 1. A direct link to this document may be found in the online article’s HTML reference section. The document may also be reached via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from [ftp.aip.org](ftp://ftp.aip.org) in the directory /epaps/. See the EPAPS homepage for more information.  
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 [31]  $N_C$  is taken as twice the number of balls in the top layer of the crystal, averaged over several snapshots well separated in time. An algorithm based on a fourfold symmetry order parameter and related criteria was employed in determining which balls were in the crystal.