P H Y S I C A L   R E V I E W   L E T T E R S

Thermodynamics and Statistical Mechanics of Dense Granular Media

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By detailed molecular dynamics and Monte Carlo simulations of a model system we show that granular materials at rest can be described as thermodynamics systems. First, we show that granular packs can be characterized by few parameters, as much as fluids or solids. Then, in a second independent step, we demonstrate that these states can be described in terms of equilibrium distributions which coincide with the statistical mechanics of powders first proposed by Edwards. We also derive the system equation of state as a function of the "configurational temperature," its new intensive thermodynamic parameter.

Granular materials, such as sand or powders, in many respects are similar to fluids or solids [1], even though in the absence of an external drive they rapidly come to rest, due to strong dissipation and negligible thermal energy scales (they are nonthermal systems), in disordered states very similar to glasses [2–7]. As standard thermodynamics is not applicable to describe them, it is natural to ask whether we can even refer to granular packs as "states." The problem of finding the correct theoretical framework where to describe granular media is in fact of deep relevance to civil engineering, geophysics, and physics [1,8–10].

Edwards proposed [11] a thermodynamic description for static granular media, which was partially investigated by recent experiments [12–14] and via the simulations of schematic models [6,7,15–20]. These experiments have established that a granular system subject to a tapping dynamics, such as subsequent mechanical oscillations of the container, may lose memory of its initial state and reach a stationary state of volume fraction only dependent on the tapping intensity, a precondition for a statistical mechanics description of static granular material to be possible. The study of out-of-equilibrium (aging) slowly sheared granular assemblies is also useful for the validation of the statistical mechanics of granular media [6], but it is inherently restricted to a small range of very high volume fractions, where the system is jammed [21].

Here we give strong evidence supporting the existence of a thermodynamical and statistical mechanical description of granular media. First, we demonstrate via molecular dynamics (MD) simulations that granular packs at rest are genuine thermodynamic states, as they are characterized by a small set of parameters regardless of the procedure with which they are generated. Then we show via Monte Carlo (MC) simulations that these states can be described in terms of the equilibrium distribution proposed by Edwards. The coincidence between time averages (MD) and ensemble averages (MC) is strong evidence in favor of the statistical mechanics approach to granular media. For details of materials and methods, see the supplementary materials available online [22].

MD simulations: Time averages.—We run molecular dynamics simulations of $N = 1600$ monodisperse spherical grains of diameter $d = 1$ cm and mass $m = 1$ g. Grains under gravity are confined in a box with a square basis of length $L = 10$ cm (see Fig. 1), with periodic boundary conditions in the horizontal directions. The bottom of the box is made of other immobile, randomly displaced grains (to prevent crystallization). Two grains in contact interact via a normal and a tangential force. The former is given by the spring-dashpot model, while the latter is implemented by keeping track of the elastic shear displacement throughout the lifetime of a contact [23,24]. The coefficient of restitution is constant, $e = 0.8$. In order to avoid the effects of the bottom and the upper free-surface, we define the volume fraction as the total volume occupied by the particles in a region enclosed between two horizontal virtual planes placed at $h_{bottom} = 2D$ and $h_{top} = z_{max} - 2D$, where z_{max} is the maximum height of a particle.

As in a recent experiment [14] the system is immersed in a fluid and, starting from a random configuration, it is subject to a dynamics made of a sequence of flow pulses where the fluid flows through the grains (see Fig. 1). In a single pulse the flow velocity, directed against gravity, is $V > 0$ for a time τ_0; then the fluid comes to rest. We model the fluid-grain interaction [25,26] via a viscous force pro-
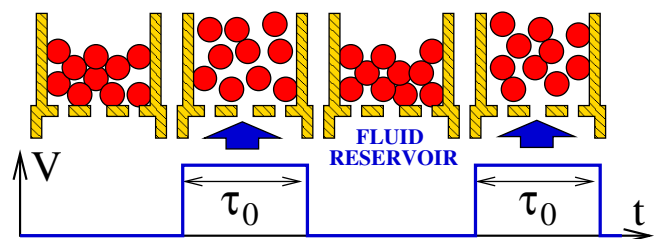

FIG. 1 (color online).   Schematic plot of the investigated system. A monodisperse 3D grains pack of spheres immersed in a fluid is subject to dynamics made of flow pulses of velocity V and duration τ_0. Before applying a pulse we wait for the pack to settle. The flow-pulse dynamics is repeated up to reach stationary conditions (see Fig. 2).

portional to the fluid-grain relative velocity: $\mathbf{F}_{fg} = -A(\mathbf{v} - \mathbf{V})$, where $\mathbf{v}$ is the grain and $\mathbf{V}$ is the fluid velocity. The prefactor $A = \gamma(1 - \Phi_l)^{-3.65}$ is dependent on the local packing fraction Φ_l in a cube of side length $3d$ around the grain, and the constant [26] is $\gamma = 1$ N s/cm.

During each pulse, grains are fluidized and then come to rest under the effect of gravity in a different mechanically stable state. The tapping dynamics, therefore, allows for the exploration of the phase space of the mechanically stable granular packs. When the system is subject to such a tap dynamics, it compactifies until it reaches a stationary state where its properties do not depend on the dynamics history. Figure 2 shows that the volume fraction of our system increases by following a stretched exponential law,

$$\Phi(t) = \Phi_\infty - (\Phi_\infty - \Phi_0)\exp[-(t/\tau)^c], \qquad (1)$$

and $c \simeq 1$, in agreement with the experiment by Philippe *et al.* [27]. The relaxation time diverges as the tapping intensity decreases, indicating the presence of a glassylike behavior which will be discussed elsewhere [28] and preventing (for computational reasons) the study of volume fractions above 0.62. As the thermodynamics approach to granular media aims to describe stationary states, all of measures shown below (averaged over 32 runs) are recorded after the application of a long sequence of flow pulses, when the system is at stationarity.

We plot in Fig. 3 the stationary values of the volume fraction $\phi(V, \tau_0)$ (measured in the bulk of the system) and its fluctuations $\Delta\phi(V, \tau_0)$ recorded after a sequence of such flow pulses of duration τ_0 and velocity V. By definition $\Delta\phi$ is the standard deviation of ϕ around its average value at stationarity, which appears to scale with the number of particles as $N^{1/2}$. Actually, the volume fraction

probability distributions is Gaussian [14,22]. ϕ decreases with V and with τ_0: the stronger the pulse, i.e., the larger V or τ_0, the looser the pack settles after it. Similarly, $\Delta\phi$ increases with V and τ_0.

Even though ϕ depends on both the parameters of the dynamics V and τ_0, we show now that such stationary states are indeed genuine ''thermodynamic states''; i.e., they can be described, in this system, by one macroscopic parameter. Actually, the upper panel of Fig. 4 shows that when $\Delta\phi$ is parametrically plotted as function of ϕ, the scattered data of Fig. 3 collapse, within numerical approximation, onto a single master function. This is a clear indication that $\Delta\phi$ and ϕ are in a one-to-one correspondence, no matter how the state with packing fraction ϕ is attained. Our claim is that such a property should be found for any macroscopic observable of the system: we checked some of them, including the energy and its fluctuations and the coordination number of grains. Actually, in the lower panel of Fig. 4 we show that the whole radial distribution function $g(r)$ of a pack is characterized only by its corresponding value of ϕ; i.e., states attained with different dynamical protocols (V, τ_0), but having the same ϕ, have the same $g(r)$. From these results we derive our first conclusion: At stationarity, we can describe the pack with only one parameter, e.g., ϕ, independently of the dynamical protocol. Such a parameter thus characterizes the thermodynamics state of the system.

MC simulations: Ensemble averages.—Our second important step is to identify the correct statistical mechanics distribution for these states. Under a very strong assumption (discussed, for instance, in [7,11,15–20,22,29–31]), Edwards proposed to use for the grains of a powder the standard machinery of statistical mechanics. He suggested, however, to consider a reduced configurational space: the
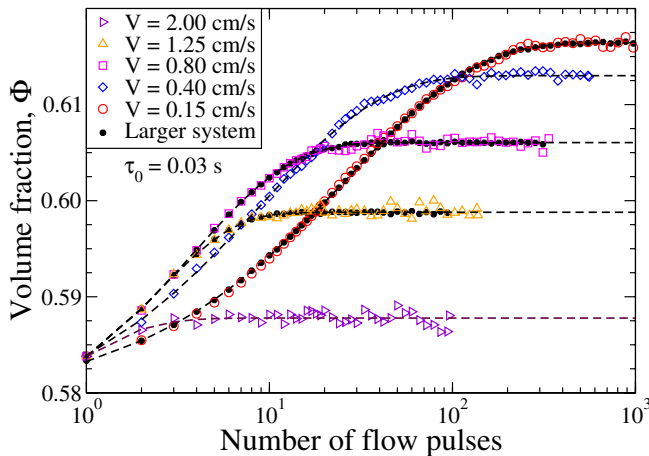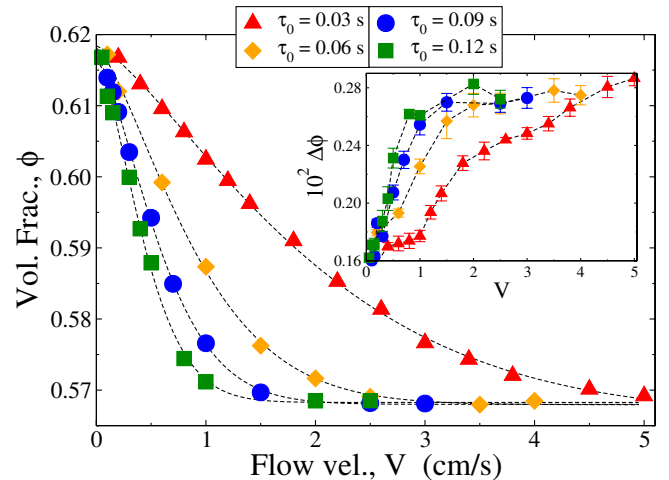

FIG. 2 (color online).   Compaction of systems subject to tapping dynamics with $\tau_0 = 0.03$ s and different values of the fluid velocity as indicated, averaged over 32 runs. Solid black circles refer to simulations with 4 times more particles, outlining the absence of finite size effects. Dashed lines are fits to a stretched exponential law [Eq. (1)].

FIG. 3 (color online).   The main panel shows the volume fraction ϕ attained at stationarity (see Fig. 2) measured when the pack is settled, as a function of V, for the shown values of τ_0: the stronger the pulses, the fluffier the pack. The inset shows the dependence of the volume fraction fluctuations on V and τ_0.
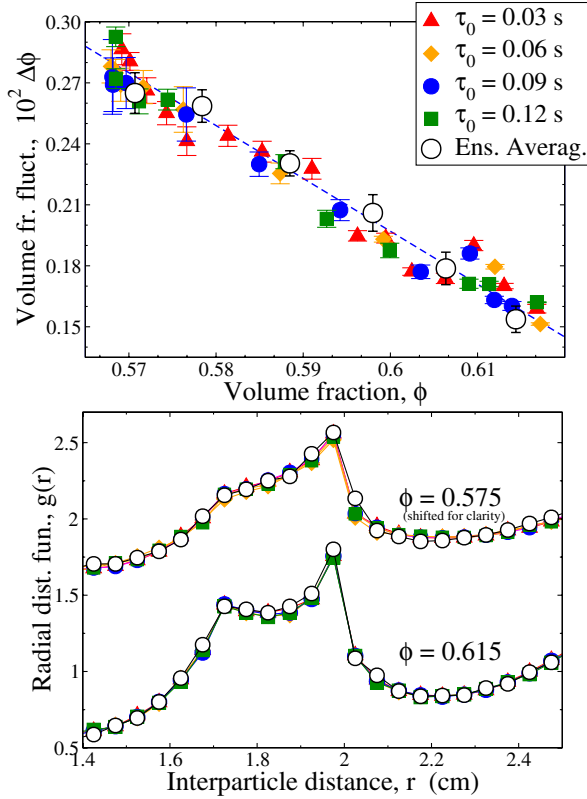
FIG. 4 (color online). (Upper panel) The $\Delta\phi$ data of Fig. 3 (same symbols are used) are here plotted as a function of ϕ: they collapse on a single master curve, showing that $\Delta\phi$ is in a one-to-one correspondence with ϕ, irrespectively of the dynamical protocol used to arrive at ϕ. The dotted line is a linear best fit. A similarly good collapse is also found (lower panel) when we plot the radial distribution function $g(r)$ for packs having the same volume fraction (the same packs of Fig. 3 are shown with the same symbols). In particular, we show $g(r)$ for $\phi = 0.615$ and $\phi = 0.575$ (shifted for clarity). The open circles in both panels are the corresponding ensemble averages independently calculated from Eq. (2): within numerical errors, they scale on the same curves, pointing out that this statistical mechanics measure is an excellent approximation of the time averages over the pulse dynamics.

system at rest (i.e., not in its "fluidized" regime) is described by a flat ensemble average restricted to its blocked configurations (i.e., its mechanically stable microstates). Under these hypotheses [16,17,22] the canonical ensemble probability P_r to find the blocked microstate r of energy E_r is

$$P_r \propto e^{-\beta_{\mathrm{conf}} E_r}, \tag{2}$$

where the inverse of β_{conf} is the conjugate parameter of the energy, called configurational temperature, T_{conf}.

In order to check whether such a statistical mechanics scenario applies, we compared ensemble averages over the distribution of Eq. (2) with those over the flow tap dynamics. For instance, the average value of ϕ over the distribution of Eq. (2) is

$$\langle\phi\rangle(T_{\mathrm{conf}}) = \frac{\sum_r \phi_r \exp(-E_r/T_{\mathrm{conf}})}{\sum_r \exp(-E_r/T_{\mathrm{conf}})}, \tag{3}$$

where the sum runs over all blocked microstates, and ϕ_r is the volume fraction of microstate r. We evaluated these ensemble averages by use of a Monte Carlo method which is an extension of that introduced in Refs. [6,18] to the frictional case [22] (frictional forces are essential to assure the stability of granular packs with small volume fraction). Figure 4 shows, as open circles, the functions $\langle\Delta\phi\rangle(\langle\phi\rangle)$ $[\langle g(r)\rangle(\langle\phi\rangle)]$ in the upper (lower) panel. These ensemble averages collapse, to a very good approximation, on the same master function of the time averaged data from the flow-pulse dynamics discussed before (notice that there are no adjustable parameters). Thus, the present statistical mechanics description appears to hold, up to the current numerical accuracy, at least as a first very good approximation. Interestingly, the off-equilibrium dynamical effective temperature defined at high volume fractions from dynamical fluctuation-dissipation relations [6] appears to coincide with the configurational temperature derived here at stationarity [22].

The function $\phi(T_{\mathrm{conf}})$, derived from the above ensemble averages, is the system equation of state. We plot $\phi(T_{\mathrm{conf}})$ in Fig. 5, where the data from MD simulations are included too by using the data collapse from Fig. 4 and integration of the static fluctuation-dissipation relations [12,14,16,17,22].

Conclusions.—Summarizing, in the present MD simulations of a nonthermal monodisperse granular system under flow pulses, we find that the stationary configurations of the system can be fully described by only one parameter, e.g., ϕ, and can be thus considered as genuine thermodynamic states. Within our numerical accuracy, we also showed that a statistical mechanics based on the
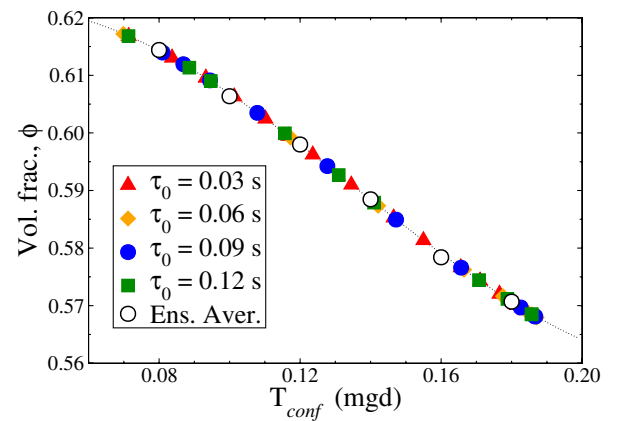

FIG. 5 (color online). The equation of state of granular materials at rest, showing the volume fraction ϕ as a function of the configurational temperature, T_{conf}. Ensemble averages are obtained via the Monte Carlo procedure, while time averages are obtained from the data of Fig. 3 via the use of the static fluctuation-dissipation relation [22].

distribution of Eq. (2) is grounded to describe these states. We could derive as well the equation of state, $\phi(T_{conf})$, of the system.

This evidence strongly supports the relevance of a fundamental theory of dense granular media and thus addresses a variety of important issues in the next future, such as response functions in a granular system, mixing or segregation phenomena, and the nature of their jamming transition and phase diagram [3,7,15,32].

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[1] H. M. Jaeger, S. R. Nagel, and R. P. Behringer, Rev. Mod. Phys. **68**, 1259 (1996).

[2] M. Nicodemi, A. Coniglio, and H. J. Herrmann, Phys. Rev. E **55**, 3962 (1997).

[3] A. J. Liu and S. R. Nagel, Nature (London) **396**, 21 (1998).

[4] *Jamming and Rheology: Constrained Dynamics on Microscopic and Macroscopic Scales*, edited by A. J. Liu and S. R. Nagel (Taylor and Francis, London, 2001).

[5] L. E. Silbert, D. Ertas, G. S. Grest, T. C. Halsey, and D. Levine, Phys. Rev. E **65**, 051307 (2002).

[6] H. A. Makse and J. Kurchan, Nature (London) **415**, 614 (2002).

[7] *Unifying Concepts in Granular Media and Glasses*, edited by A. Coniglio, A. Fierro, H. J. Herrmann, and M. Nicodemi (Elsevier, Amsterdam, 2004).

[8] *Powders and Grains*, edited by R. P. Behringer and J. T. Jenkins (Balkema, Rotterdam, 1997), Vol. 97.

[9] R. M. Nedderman, *Statics and Kinematics of Granular Materials* (Cambridge University Press, Cambridge, England, 1992).

[10] T. Siegfried, Science **309**, 76 (2005).

[11] S. F. Edwards and R. B. S. Oakeshott, Physica (Amsterdam) **157A**, 1080 (1989).

[12] J. B. Knight, C. G. Fandrich, C. N. Lau, H. M. Jaeger, and S. R. Nagel, Phys. Rev. E **51**, 3957 (1995).

[13] E. R. Nowak, J. B. Knight, M. L. Povinelli, H. M. Jaeger, and S. R. Nagel, Powder Technol. **94**, 79 (1997).

[14] M. Schröter, D. I. Goldman, and H. L. Swinney, Phys. Rev. E **71**, 030301(R) (2005).

[15] P. Richard, M. Nicodemi, R. Delannay, and P. Ribière, Nat. Mater. **4**, 121 (2005).

[16] A. Coniglio and M. Nicodemi, Physica (Amsterdam) **296A**, 451 (2001).

[17] A. Fierro, M. Nicodemi, and A. Coniglio, Europhys. Lett. **59**, 642 (2002).

[18] A. Barrat, J. Kurchan, V. Loreto, and M. Sellitto, Phys. Rev. Lett. **85**, 5034 (2000).

[19] J. J. Brey, A. Padros, and B. Sanchez-Rey, Physica (Amsterdam) **275A**, 310 (2000).

[20] D. S. Dean and A. Lefèvre, Phys. Rev. Lett. **86**, 5639 (2001).

[21] F. Q. Potiguar and H. A. Makse, Eur. Phys. J. E **19**, 171 (2006).

[22] See EPAPS Document No. E-PRLTAO-97-045642 for (1) volume fraction fluctuations at stationarity; (2) description of the statistical mechanics approach to granular media; (3) comparison of our approach (configurational temperature) to that of Ref. [6] (dynamical temperature); (4) explanation of the Monte Carlo method. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

[23] L. E. Silbert *et al.*, Phys. Rev. E **64**, 051302 (2001).

[24] We use the model "$L3$" described in detail in Ref. [23].

[25] P. Sánchez, M. R. Swift, and P. J. King, Phys. Rev. Lett. **93**, 184302 (2004).

[26] C. Crowe, M. Sommerfeld, and Y. Tsuji, *Multiphase Flows with Droplets and Particles* (CRC Press, Boca Raton, FL, 1998).

[27] P. Philippe *et al.*, Europhys. Lett. **60**, 677 (2002).

[28] M. Pica Ciamarra, M. Nicodemi, and A. Coniglio (to be published).

[29] I. K. Ono *et al.*, Phys. Rev. Lett. **89**, 095703 (2002).

[30] D. De Smedt, C. Godrèche, and J. M. Luck, Eur. Phys. J. B **32**, 215 (2003).

[31] G. Tarjus and P. Viot, Phys. Rev. E **69**, 011307 (2004).

[32] E. I. Corwin, H. M. Jaeger, and S. R. Nagel, Nature (London) **435**, 1075 (2005).