Entropy of Jammed Matter

Christopher Briscoe, Chaoming Song, Ping Wang, and Hernán A. Makse
Levich Institute and Physics Department, City College of New York, New York, New York 10031, USA
(Received 18 June 2008; published 31 October 2008)

We investigate the nature of randomness in disordered packings of frictional spheres. We calculate the entropy of 3D packings through the force and volume ensemble of jammed matter, a mesoscopic ensemble and numerical simulations using volume fluctuation analysis and graph theoretical methods. Equations of state are obtained relating entropy, volume fraction and compactivity characterizing the different states of jammed matter. At the mesoscopic level the entropy vanishes at random close packing, while the microscopic states contribute to a finite entropy. The entropy of the jammed system reveals that the random loose packings are more disordered than random close packings, allowing for an unambiguous interpretation of both limits.

DOI: 10.1103/PhysRevLett.101.188001 PACS numbers: 81.05.Rm

Filling containers with balls is among the oldest physical puzzles known to scientists [1]. Apart from its mathematical significance, this problem has found applications in modern topics, such as jamming in granular media, colloids, and the structure of liquids and the glass transition [2]. Despite vast progress made in developing a statistical mechanics for such systems [3], basic questions remain unanswered, including [1,4,5]: What is a jammed state and how do we characterize its state of randomness?

In an attempt to rigorously define the jammed states, Torquato and co-workers have proposed three categories of jamming [6]: locally, collectively, and strictly jammed. This problem is intimately related to the existence of well-defined upper and lower limits in the density of disordered packings, random close packing (RCP), and random loose packing (RLP) [1], a longstanding open question in the field. A definition of RCP requires proper definitions of *jammed states* and the concept of *randomness* [5]. These previous definitions of jamming are based purely on geometrical considerations, sufficient to describe frictionless grains [6] but not for granular materials where friction dominates [7]. Figure 1(a) illustrates the point: a frictionless hard sphere system is not locally jammed if only normal forces are considered, since the ball can freely move in the vertical direction. The same geometrical configuration is locally jammed if friction is allowed between the particles, revealing the importance of forces in the definition of jamming for frictional particles.

The goal of the present Letter is to characterize jamming and the degree of randomness for frictional hard spheres and obtain equations of state. Our framework is rooted in statistical mechanics and considers calculation of the entropy at the volume-force (V-F) ensemble level [3] through force and torque balance conditions. The simulations and theory developed allow understanding of the qualitative behavior of equations of state relating volume fraction, entropy and compactivity, and illuminate the nature of RCP and RLP. We follow three complementary approaches to characterize the entropy of jammed matter. (i) Computer studies: We first investigate frictional packings of spheres at the jamming transition numerically. We compute the equations of state, entropy, and compactivity, as a function of volume fraction, ranging from RLP to RCP. The entropy is calculated by two numerical methods; direct analysis of volume fluctuations via a fluctuation-dissipation theorem and graph theoretical methods. Simulations show that random loose packings are more disordered and have higher compactivity than random close packings. In order to rationalize the simulation results we follow two theoretical approaches: (ii) We develop the concept of randomness in the V-F ensemble following the Gibbs distribution [3], which is different from the measurement of randomness of a single packing in terms of an ensemble of order parameters [5]. Since analytical expressions of the entropy are difficult to obtain in this ensemble we develop, (iii), a mesoscopic ensemble approximation [8] based on mechanical equilibrium imposing an average coordination number, Z, larger or equal than the minimum isostatic coordination as conjectured by Alexander [9] (see also [7,10–13]). Calculations are done under the mesoscopic approximations of [8] giving rise to a mesoscopic configurational entropy, achieving a minimal value at RCP and maximal value at RLP. The results characterize the disorder of RCP and RLP at the mesoscopic level in general agreement with the simulations. They also suggest that the configurational entropy requires augmentation to include the entropy of the microscopic states neglected at the mesoscopic level.

Numerical simulations.—We investigate computer generated packings of 10 000 spherical equal-size particles of 100 μm diameter interacting via Hertz (normal) and Mindlin (tangential) contact forces (with shear modulus 29 GPa and Poisson's ratio 0.2) with Coulomb friction, μ, using methods previously developed in [8,11]. Packings characterized by different μ are generated by compressing a gas of particles from an initial (unjammed) density, ϕ_i, with a compression rate, Γ, until a final density, ϕ, at the jamming transition.

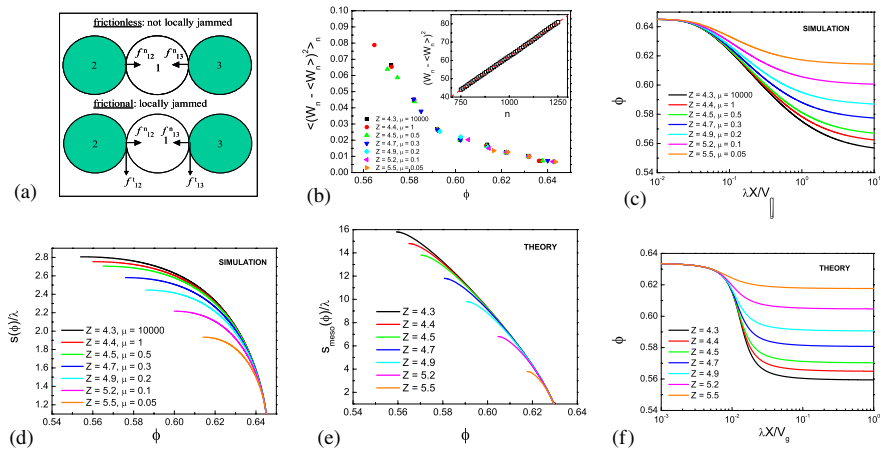

FIG. 1 (color online). Numerical and theoretical results. (a) A disk in two dimensions under mechanical equilibrium by two nearest neighbor contacts. The disk is not jammed under a normal force interaction, but it jams when tangential forces are present. (b) $\langle \Delta \mathcal{W}_n^2 \rangle_n$ versus ϕ. Inset shows the extensivity of $\langle \Delta \mathcal{W}_n^2 \rangle$ versus n. (c) ϕ versus X from the integration of (b). (d) Entropy versus ϕ from the integration of (c). Entropy at RCP achieves a value of 1.1λ as calculated by the Shannon entropy at RCP. (e) Prediction of the mesoscopic theory for $s_{\mathrm{meso}}(\phi)/\lambda + 1.1$. (f) Prediction of the mesoscopic theory for $\phi(X)$.

The friction μ ranges from 0 to ∞ producing packings with coordination number varying from $Z \approx 6$ to $Z \approx 4$, respectively. Thus, the preparation protocol produces packings with densities parameterized by $\phi(\mu, \Gamma, \phi_i)$. In general, the lower Γ the smaller the obtained ϕ, while the larger ϕ_i the larger ϕ of the packing. We also find that under our numerical protocol there exits a common function $Z(\mu)$ over the different Γ and ϕ_i (see [8]). For $\mu \to \infty$, ϕ ranges from the RLP limit $\phi_{\mathrm{RLP}} \approx 0.55$ obtained when $\Gamma \to 0$ and $\phi_i < 0.55$ to the RCP limit $\phi_{\mathrm{RCP}} \approx 0.64$ obtained for larger Γ and $\phi_i \to 0.64$ (note that merely changing Γ is not sufficient to allow ϕ_{RCP} to approach 0.64, as discussed in [8], for $\mu \to \infty$). For $\mu = 0$, the density is approximately $\phi \approx \phi_{\mathrm{RCP}}$ for any (Γ, ϕ_i). For intermediate μ, the packings follow the phase diagram as obtained in [8].

The calculation of the entropy as a function of volume fraction is realized by using volume fluctuation analysis through a fluctuation-dissipation relation [14] complemented with graph theoretical methods [15,16]. We first define the Voronoi cell associated with each particle i and calculate its Voronoi volume $\mathcal{W}_i$. We then perform statistical analysis of the volume fluctuations by considering a cluster of n contacting particles with volume $\mathcal{W}_n = \sum_i^n \mathcal{W}_i$. We calculate the average volume, $\langle \mathcal{W}_n \rangle$ and fluctuations $\langle (\mathcal{W}_n - \langle \mathcal{W}_n \rangle)^2 \rangle$, where $\langle \cdot \rangle$ is an average over many n clusters. We find that for sufficiently large $n \approx 1000$, contrasting the results of [17], the fluctuations scale with n and therefore are extensive and well defined [see inset of Fig. 1(b)].

From the large n behavior we extract the fluctuations, plotted in Fig. 1(b), versus ϕ for every packing studied. The compactivity of the packing, X, is obtained via the integration of the fluctuation relation $\langle (\mathcal{W}_n - \langle \mathcal{W}_n \rangle)^2 \rangle = \lambda X^2 d\langle \mathcal{W}_n \rangle / dX$ as $X^{-1} = \lambda \int_{\phi(X)}^{\phi_{\mathrm{RLP}}} d\langle \mathcal{W}_n \rangle / \langle (\mathcal{W}_n - \langle \mathcal{W}_n \rangle)^2 \rangle$, where we use that $\phi(X \to \infty) \to \phi_{\mathrm{RLP}}$ [8], and λ is the analogue of the Boltzmann constant. Since Voronoi volumes are additive, $\langle \mathcal{W}_n \rangle = \langle \mathcal{W} \rangle = N V_g / \phi$, where V_g is the volume of the grain. Therefore, the above integration is rewritten as

$$(X/V_g)^{-1} = \lambda \int_{\phi_{\mathrm{RLP}}}^{\phi(X)} d\phi / (\phi^2 \langle (\mathcal{W}_n - \langle \mathcal{W}_n \rangle)^2 \rangle_n), \quad (1)$$

where $\langle (\mathcal{W}_n - \langle \mathcal{W}_n \rangle)^2 \rangle_n$ is the fluctuation density. We may then utilize the fluctuation density as a function of ϕ, shown in Fig. 1(b), and integrate along a line of constant $Z(\mu)$. We note that while the fluctuation densities for all $Z(\mu)$ in this study collapse onto a single curve, illustrated in Fig. 1(b), the limit of integration, ϕ_{RLP} in Eq. (1), changes as discussed in the phase diagram of [8], increasing as μ decreases.

The equation of state, $\phi(X)$, is plotted in Fig. 1(c) for different values of the average coordination number of the packings, $Z(\mu)$, revealing that as we approach $\phi_{\mathrm{RCP}} \approx 0.64$, $X \to 0$, regardless of the value of μ. Further, $X \to \infty$ as we approach ϕ_{RLP}, with the smallest volume fraction of the RLP appearing for $\mu \to \infty$ and $Z \approx 4$, with $\phi_{\mathrm{RLP}} \approx 0.55$.

The entropy, S, and its density, $s = S/N$, are obtained by integrating $(X/V_g)^{-1} = -\phi^2 \partial s / \partial \phi$, as

$$s(\phi) - s(\phi_{\mathrm{RCP}}) = \lambda \int_{\phi}^{\phi_{\mathrm{RCP}}} d\phi / [(X(\phi)/V_g)\phi^2]. \quad (2)$$

This analysis provides the entropy up to a constant of integration $s(\phi_{\mathrm{RCP}})$. To obtain an estimation of the entropy of RCP we use an independent method based on information theory [15,16]. We use the Voronoi cell and Delaunay triangulation for each particle to define a Voronoi network. We construct a graph as a cluster of n contacting particles which, by means of graph automorphism, can be transformed into a standard form or "class" i of topologically equivalent graphs considered as a state with an occurrence $p(i)$. In practice, we determine $p(i)$ by extracting a large number m of clusters of size n from the system and count the number of times, f_i, a cluster i is observed, such that: $p(i) = f_i/m$. The Shannon entropy of a clusters of size n is $H(n) = -\lambda \sum p(i) \ln p(i)$, and the entropy density is $s = \lim_{n \to \infty} [H(n+1) - H(n)]$, converging so rapidly that even moderate values of n are enough to obtain a sufficient approximation of s [16]. The Shannon entropy density provides an estimation of the entropy for the RCP state,

$s(\phi_{\mathrm{RCP}}) \approx 1.1\lambda$, serving as the constant of integration for the entropy density as realized by volume fluctuations. The resulting entropy density is plotted in Fig. 1(d) versus ϕ for different $Z(\mu)$.

When comparing all packings with different $Z(\mu)$ and ϕ, the maximum entropy is at the minimum volume fraction of RLP $\phi_{\mathrm{RLP}} \approx 0.55$ when $X \to \infty$ at infinite friction. The minimum entropy is found for the RCP state at $\phi_{\mathrm{RCP}} \approx 0.64$ for $X \to 0$, for all the values of friction, indicating the degeneracy of the RCP state, contrary to the common belief that the RCP limit corresponds to a state with the highest number of configurations and therefore the highest entropy.

Statistical mechanics of frictional hard spheres.—Next, we use the ensemble of jammed matter to rationalize the obtained equations of state [3]. Experiments of shaken grains, fluidized beds and oscillatory compression of grains [14] indicate that granular materials show reversible behavior, and the analogue of the conserved energy, E, in thermal systems is the volume $V = NV_g/\phi$, for a system with N at positions $\vec{r}_i$. Thus, the number of configurations, Ω, and the entropy in the microcanonical ensemble of jammed hard spheres is defined as [3]

$$\Omega(V) = e^{S(V)/\lambda} = \int \delta(V - \mathcal{W}(\vec{r}_i))\Theta_{\mathrm{jam}}(\vec{r}_i)\mathcal{D}\vec{r}_i. \quad (3)$$

Just as $\partial E/\partial S = T$ is the temperature in equilibrium system, the "temperature" in granular matter is $X = \partial V/\partial S$. Here $\Theta_{\mathrm{jam}}(\vec{r}_i)$ is a constraint function restricting the integral to the ensemble of jammed states, $\mathcal{W}(\vec{r}_i)$ is the volume function associated with each particle taking the role of the Hamiltonian. The crux of the matter is then to properly define Θ_{jam} and $\mathcal{W}$ to calculate the entropy and volume in the ensemble of jammed matter.

Volume and force V-F ensemble.—A minimum requirement of $\Theta_{\mathrm{jam}}(\vec{r}_i)$ is to ensure touching grains, and obedience to Newton's force and torque laws. As in the numerical simulations, the volume function, $\mathcal{W}(\vec{r}_i)$, is taken as the volume of the Voronoi cell associated with each particle at position $\vec{r}_i$, for which an analytical form has been obtained in [8]. Following Eq. (3), the entropy in the V-F ensemble of frictional hard spheres takes the form:

$$\Omega_{\text{V-F}} = e^{S(V)/\lambda} = \int \delta(V - \mathcal{W}(\vec{r}_i)) \prod_i \left\{ \delta\left(\sum_{j\neq i} \vec{f}_{ij}\right) \delta\left(\sum_{j\neq i} \vec{f}_{ij} \times \vec{r}_{ij}\right) \delta(\vec{f}_{ij} - \vec{f}_{ji}) \prod_{j\neq i} [\Theta(\mu f_{ij}^N - f_{ij}^T)\delta([(\vec{r}_{ij})^2 - 1])\mathcal{D}f_{ij}]\mathcal{D}r_i \right\}, \quad (4)$$

where $\vec{r}_{ij} \equiv \vec{r}_i - \vec{r}_j$, the normal interparticle force is $f_{ij}^N \equiv |\vec{f}_{ij} \cdot \hat{r}_{ij}|$, the tangential force: $f_{ij}^T \equiv |\vec{f}_{ij} - (\vec{f}_{ij} \cdot \hat{r}_{ij})\hat{r}_{ij}|$. All quantities are assumed properly a dimensional for simplicity of notation. The terms inside the brackets $\{\cdot\}$ correspond to the jamming constraint function Θ_{jam} in Eq. (3), and therefore define the ensemble of jammed states. The first three δ-functions inside the big brackets impose Newton's second and third law. The Heaviside Θ-function imposes the Coulomb condition and the last δ-function imposes the touching grain condition for hard spheres, assuming identical grains of unit diameter. Integration is over all forces and positions which are assumed to be equally probable as in the flat average assumption of the microcanonical ensemble.

The conditions specified in Eq. (4) are met in the numerical packings; thus, the results of Figs. 1(b)–1(d) can be interpreted as the ensemble average of Eq. (4) under assumption of uniformity in the jammed configurations. However, Eq. (4) is difficult to solve. Analytical progress can be done by considering a coarse graining of the Voronoi volume function and working with mesoscopic theory [8] to obtain a configurational entropy at the mesoscopic level.

Coordination number Z ensemble.—Simple counting arguments, neglecting correlations between nearest neighbors, consider that a necessary condition for mechanical equilibrium is that the number of independent force variables must be larger or equal than the number of linear independent force-torque balance equations. Alexander [9] conjectured that at the transition point for frictionless spherical packings [9,13] the system is exactly isostatic with a minimal coordination, $Z = 2d = 6$ in three dimensions. Such a conjecture can be extended to the infinite friction case, where $Z = d + 1 = 4$ [13]. In the presence of finite interparticle friction coefficient μ, the analytic form of $Z(\mu)$ is difficult to achieve since the counting argument involves nonlinear inequality constraints through the Coulomb condition. Despite the theoretical difficulty, there exists a dependency of Z with μ suggested by simulations [7,8,12].

We consider a mesoscopic free volume function coarse-grained over a few coordination shells that reduces the degrees of freedom to the coordination number z' as shown in [8]: $w(z') = \frac{2\sqrt{3}}{z'} V_g$. The $w(z')$ function is calculated [8] by obtaining the probability distribution of Voronoi volumes associated with a particle in the jammed state. This probability is decomposed into a bulk term depending on w and a contact term depending on z'. Note that z' refers to geometrical contacts that may carry no forces and can be larger than the mechanical coordination Z given by the isostatic condition: $Z < z'$ [8].

The mesoscopic approximation refers to the use of such a mesoscopic free volume function in the partition function, taking into account the effect of the environment of a particle rather than the particle itself. Thus, we can reduce the partition function to a single noninteracting particle. The mesoscopic entropy density is obtained in the canonical ensemble [3,8]:

$$s_{\mathrm{meso}} = \langle w \rangle/\lambda X + \lambda \ln \int_{Z(\mu)}^{6} g(z') \exp\left(-\frac{w(z')}{\lambda X}\right) dz', \quad (5)$$

where the isostatic condition enters through the limit of integration. The space of configurations is considered discrete since the states are collectively jammed [6]. If the typical distance between states is h_z, the density of states is $g(z') \propto h_z^{z'}$ analogous to discretization of phase space imposed by the Heisenberg principle with density of states h^{-d}, where h is the Planck constant. Equation. (5) is a coarse-grained mesoscopic form of the full entropy in Eq. (4) reducing the degrees of freedom to z. Thus the effective ''Plank constant'' h_z appears in Eq. (5) and not in Eq. (4).

The mesoscopic entropy of Eq. (5) is plotted in Fig. 1(e) as a function of ϕ for different values of Z. We see that it captures the general behavior found in the simulations, i.e., maximal at RLP for $Z = 4$ and minimal at RCP. Furthermore, all the curves for different Z approach $S \sim \ln X$ as $X \to 0$, similar to a thermal ideal gas. We conclude that, at the mesoscopic level, the entropy vanishes at RCP (in fact it diverges to $-\infty$ when $\phi \to \phi_{\mathrm{RCP}}$ closer than a constant proportional to h_z), providing a characterization of RCP. This result qualitatively resembles behavior of the complexity of the jammed state in the replica approach to jamming [18]. We use $h_z = 0.01$ in Fig. 1(e) such that the mesoscopic entropy vanishes very close to the predicted value of $\phi_{\mathrm{RCP}} \approx 0.634$ [8] and the value of the microscopic entropy as calculated via graph theoretical methods. The value of h_z is chosen to fit the theory with simulation as close as possible, where the only constraint imposed by theory is $h_z < 1$. An important result is the direct implication of a larger number of states available to jammed systems at RLP with respect to any higher volume fraction.

It is possible to interpret the RCP as a Kauzmann point (K point) [18] in analogy with the density (temperature) at which the configurational entropy of a colloidal (molecular) glass vanishes at the ideal glass transition.

We augment the mesoscopic entropy with the entropy of the microscopic states to obtain the full entropy as $s = s_{\mathrm{meso}} + s_{\mathrm{micro}}$. Since for frictionless packings s_{meso} vanishes, then $s = s_{\mathrm{micro}}$, implying that we can obtain s_{micro} from the full entropy of the K point as calculated numerically. Therefore, Fig. 1(e) is plotted as $s_{\mathrm{meso}}/\lambda + 1.1$ to obtain a plot of the full entropy to compare with the full ensemble Eq. (4) and simulations. This constant is obtained from the value given by the Shannon entropy, regarded as the entropy of RCP, which is 1.1λ.

In summary, a notion of jamming is presented that applies to frictional hard spheres, as well as frictionless ones. The entropy reveals interesting features of the RCP and RLP states such as the fact that RLP is maximally random with respect to RCP and that both limits can be seen in terms of the entropy and equation of state. The theoretical model captures the shape of the entropy and the equation of state, but not the actual values at RLP. Future study will be devoted to capture the volume fluctuations not only at the mesoscopic level but also at the microscopic level neglected in the present theory, which may lead to an understanding of the finite value of entropy found at RCP in the numerics. The agreement between theory and simulation is sufficient to indicate that the methods presented herein are appropriate for evaluating the entropy of jammed matter allowing the characterization of the state of randomness of RLP and RCP. We note that an interesting recent work [19] finds random very loose packings with negative effective temperature in an energy ensemble approach. Such states (analogous to negative X in the volume ensemble) are discussed elsewhere [8]. Our results are in general agreement with those of [20].

We thank the financial support of the NSF and DOE, Office of Basic Energy Sciences.

[1] J. D. Bernal, Nature (London) **185**, 68 (1960).
[2] *Unifying Concepts in Granular Media and Glasses* edited by A. Coniglio, A. Fiero, H. J. Herrmann, and M. Nicodemi (Elsevier, Amsterdam, 2004).
[3] S. F. Edwards and R. B. S. Oakeshott, Physica (Amsterdam) **157A**, 1080 (1989).
[4] J. G. Berryman, Phys. Rev. A **27**, 1053 (1983).
[5] S. Torquato, T. M. Truskett, and P. G. Debenedetti, Phys. Rev. Lett. **84**, 2064 (2000).
[6] S. Torquato and F. H. Stillinger, J. Phys. Chem. B **105**, 11 849 (2001).
[7] T. Unger, J. Kertesz, and D. E. Wolf, Phys. Rev. Lett. **94**, 178001 (2005).
[8] C. Song, P. Wang, and H. A. Makse, Nature (London) **453**, 629 (2008).
[9] S. Alexander, Phys. Rep. **296**, 65 (1998).
[10] C. S. O'Hern, S. A. Langer, A. J. Liu, and S. R. Nagel, Phys. Rev. Lett. **88**, 075507 (2002).
[11] H. A. Makse, D. L. Johnson, and L. M. Schwartz, Phys. Rev. Lett. **84**, 4160 (2000).
[12] L. E. Silbert *et al.*, Phys. Rev. E **65**, 031304 (2002).
[13] *Stealing the Gold: a Celebration of the Pioneering Physics of Sam Edwards*, edited by P. M. Goldbart, N. Goldenfeld, and D. Sherrington (Oxford Science Publications, Oxford, 2004).
[14] E. R. Nowak, J. B. Knight, E. BenNaim, H. M. Jaeger, and S. R. Nagel, Phys. Rev. E **57**, 1971 (1998); H. A. Makse and J. Kurchan, Nature (London) **415**, 614 (2002); M. Schröter, D. I. Goldman, and H. L. Swinney, Phys. Rev. E **71**, 030301(R) (2005).
[15] C. E. Shannon, Bell Syst. Tech. J. **27**, 379 (1948).
[16] R. L. C. Vink and G. T. Barkema, Phys. Rev. Lett. **89**, 076405 (2002); J. Brujić, C. Song, P. Wang, C. Briscoe, G. Marty, and H. A. Makse, Phys. Rev. Lett. **98**, 248001 (2007).
[17] F. Léchenault, O. Dauchot, and E. Bertin, J. Stat. Mech. (2006) P07009.
[18] G. Parisi and Zamponi, J. Chem. Phys. **123**, 144501 (2005); F. Krzakala and J. Kurchan, Phys. Rev. E **76**, 021122 (2007).
[19] M. P. Ciamarra and A. Coniglio, Phys. Rev. Lett. **101**, 128001 (2008).
[20] A. V. Anikeenko, N. N. Medvedev, and T. Aste, Phys. Rev. E **77**, 031101 (2008).