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Chapter 3

On entropic characterization of granular materials

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This chapter presents recent developments in entropic characterization of granular materials. The advantages of the formalism and its use are illustrated for calculation of structural characteristics, such as porosity fluctuations and the throat size distribution. I discuss the relations between the entropic formalism and stress transmission. It is argued that a new sub-ensemble of loading distributions is necessary, which introduces a tensor temperature-like quantity named angoricity.

1. Introduction: the entropic formalism

The introduction of statistical mechanical methods to analyse assemblies of granular systems has led to the development of new concepts in the field. Most notable are the concepts of compactivity, the analogue of temperature, and of a volume function, the analogue of the Hamiltonian. The approach is based on a description of the entropy of the granular structure, namely, the statistics of configurations that a collection of grains can assume, given that they are confined to a container of a given volume V. This approach, developed originally by Edwards and collaborators,[1] has been prompted by experimental observations[2] of a reversible behaviour of post-vibrated granular beds (albeit with intriguing irreversible precursors). The reversibility, and more importantly the reproducibility of measurements of bulk properties, suggest the existence of an ensemble of equilibrium-like configuration states. Further support for the approach has come from numerical simulations.[3]

The formalism has many parallels with conventional statistical mechanics

of thermodynamic systems. A central concept is a partition function

$$Z = \int e^{-\mathcal{W}(\{q\})/X} \Theta\left(\{q\}\right) D\{q\} \equiv e^{-Y/X} \ , \tag{1}$$

that depends on: $\{q\}$ - a complete set of degrees of freedom (DOF); $\mathcal{W}$ - a volume function that is the analogue of the Hamiltonian in thermodynamic systems and which depends on the DOF; $\Theta\left(\{q\}\right)$ - a probability density that describes the statistics of the DOF and imposes the constraint that the structure remain connected. Once these constraints, embodied in the form of δ-functions, are satisfied, the function Θ can be regarded as the conventional density of states. The scalar $X \equiv 1/\beta$, named compactivity,[1] is the analogue of the temperature. The analogue of the free energy, named the free porosity, is $Y = -\ln Z/\beta$[4].[5] The configurational entropy is $S = \beta^2 \partial Y/\partial\beta$ and the mean porosity is $V = Y + XS = \partial(\ln Z)/\partial(\beta)$. Using this formalism, many other parallels can be, and have been, made between thermodynamic systems and granular systems.

In spite of experimental and numerical testimonials, the general applicability of this approach has been controversial. In particular, it has not been clear how the idea of volumetric entropy can be used to understand macroscopic properties of granular systems. Nevertheless, the prospect of harnessing the power of statistical mechanical methods to the difficult problem of granular systems has been very appealing.

In addition to lingering skepticism, a significant hurdle to a regular use of the formalism has been the lack of a suitable explicit volume function $\mathcal{W}$ that is both rigorously additive when summed over all grains and convenient for analytical and computational purposes. As a result, several approximations have been used in the literature, leading to model-sensitive results. The form of the volume function is significant both because it is the vehicle for the derivation of explicit estimates of structural properties and because it identifies the phase space that defines the structure of granular systems. This problem has been resolved recently both in 2D[4] and in 3D,[5] with the introduction of a new partition of he granular space. In this description, grains are replaced by representative polyhedra (polygons in 2D), constructed from the contact network of the original grains. The grain polyhedra surround cell polyhedra that represent the pores of the original structure. This description makes it possible to tessellate the space by topologically identical units, called quadrons.[5] The details of the constructions and the tessellations are explained in figures 1 (2D) and 2 (3D) and their captions. In terms of these, a volume function can be identified

as a sum over quadron volumes[6]

$$W = \sum_q V_q \ . \tag{2}$$

The quadrons are the fundamental volume elements. A z-coordinated grain in 3D (2D) can be regarded as a composite of several quadrons - z in 2D and $6(z-2)$ in 3D, a picture reminiscent of quarks in elementary particles.

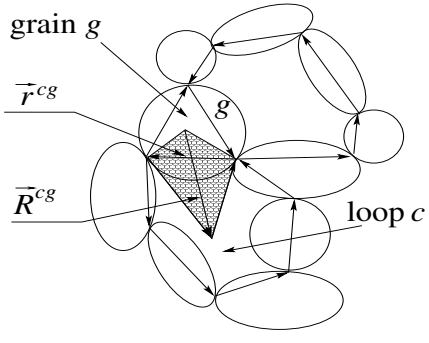

Fig. 1. The geometric construction around grain g in 2D. The vectors $\vec{r}^{cg}$ connect contact points clockwise around each grain anticlockwise around each void. The vectors $\vec{R}^{cg}$ connect from grain centres to loop centres. The shaded quadrilateral is the quadron associated with cg.

This construction resolves the problems of disentangling the geometrical correlations and identifying the DOF that describe the structure[4,5]. The polyhedra are defined by their edge vectors $\vec{r}$. Structural correlations arise from irreducible loops, each giving a dependent vector. The number of these loops is straightforward to calculate in 2D, using Euler's relation,[9] but not in 3D. These calculations are shown below.

Another advantage of this description is that it allows a local characterization of the structure by a fabric tensor, as described in[4] (2D) and in[5,10] (3D). The fabric tensors are useful both for quantifying the quadron volumes and for modelling stress transmission in granular assemblies.[11] As such, these tensors are natural descriptors of granular systems.

2. Calculations of volume-based structural properties

Two dimensions

Let $V = \mathcal{W}(\{q\})$ be the volume function of a system of N grains, described

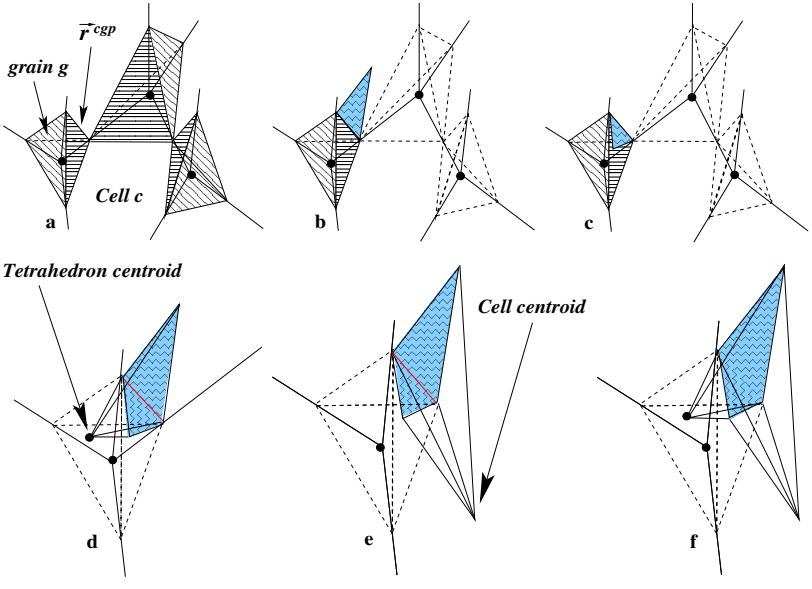

Fig. 2. The polyhedral representation in 3D. The edge vectors $\vec{r}^{cgp}$ connect contact points around grains and the construction of a 3D quadron is shown in stages. The quadrons are non-convex octahedra (shown in f) that tessellate the space perfectly. Grain volumes are composites of quadrons.

by (2), which depends on a set of structural DOF $\{q\}$. The partition function is

$$Z = \int e^{-\beta \mathcal{W}(\{q\})} \mathcal{P}(\{q\}) D\{q\} \ , \tag{3}$$

where $\mathcal{P}(\{q\})$ is the density of states, i.e. the probability density of occurrence of particular configurations of $\{q\}$. Given a mean coordination number $\bar{z}$, there are $\bar{z}N/2$ contacts and $\bar{z}N$ vectors $\vec{r}$. On using Euler relation, this gives $\bar{z}/2$ irreducible loops, leaving $\bar{z}N$ DOF. Interestingly, this is also the number of quadrons and one can use the quadron volumes, V_q, to span the phase space.

Absence of data for $\mathcal{P}(\{q\})$ led to several approximations[4,5] but a recent study of it[12] has revealed complex structure. In foam-like structure $\mathcal{P}(\{q\})$ is fitted well by a gamma distribution,

$$\mathcal{P}(V_q) = \frac{b^a V_q^{a-1}}{\gamma(a, bV_{max}) - \gamma(a, bV_{min})} e^{-bV_q} \quad ; \quad V_{min} \le V_q \le V_{max} \ , \tag{4}$$

where $V_{max} \gg 1/b$, b is the inverse of a typical quadron volume and $3 < a < 4$ and $\gamma(a, A)$ is the incomplete gamma function.[13] An 'ideal quadron-gas approximation' of uncorrelated quadrons gives

$$Z = \left[\int_{V_{min}}^{V_{max}} \mathcal{P}(V_q) e^{-\beta V_q} dV_q \right]^{\bar{z}N} . \tag{5}$$

Any volume-based structural property can be computed directly from (5).

Three dimensions

Euler relation is insufficient to determine the number of DOF in 3D. For illustration, consider foam-like structures, where every grain has $z = 4$ and is represented by a tetrahedron.[5] Seen from within a pore, the 'surface' of a cell is made of the triangular faces of the n_g^c grains surrounding it, of the contacts between the triangles and of the n_f^c faces that the triangles enclose. The latter are the 'throats' that connect to neighbour cells. There are $3n_g^c/2$ contacts and $3n_g^c$ edges on the surface, which, on using Euler relation, gives that a cell has $n_f^c = 2 + n_g^c/2$ throats. Summing over all cells, remembering that every throat is shared between two cells, gives that there are $N_f = N + N_c$ throats, or $2(1 + N/N_c)$ throats per cell.

Every polyhedron edge is a 3D vector. The polyhedron of a z-coordinated grain has $2(z-2)$ triangular faces and $3(z-2)$ edge vectors. The inter-dependency of all the edge vectors is due to geometric correlation. As in 2D, every irreducible loop obviates one vector. In foam-like structures, three of the six edge vectors of every tetrhedron are dependent. Additionally, each of the $N + N_c$ throats introduces a dependent vector. Therefore, there are in total $6N - 3N - N_f = 2N - N_c$ independent vectors, or

$$\frac{N_{dof}}{N} = \frac{3(2N - N_c)}{N} = 3\left(2 - \frac{N_c}{N}\right) \tag{6}$$

DOF per grain. Unlike in 2D, this value is significantly lower than the number of quadrons per grain.

The ratio N_c/N is a key quantity. For infinitely rough convex particles, it can be bounded by using the dual structure. In this structure, the duals of the grain polyhedra are the cell polyhedra and visa versa. The contact surfaces between the dual grains are the original throats. In 2D the dual of a statically determinate such structure is also statically determinate, but for frictionless grains, and it is plausible that the same applies in 3D. In general, the larger is z in the original system, the smaller the mean coordination number of the dual structure and visa versa. The lowest value that $\bar{z}$ can assume is determined by the condition of mechanical equilibrium

for infinitely rough grains, $\bar{z} \geq 4$.[14] The lowest mean coordination number for frictionless non-spherical grains is 12.[14] This corresponds to the number of faces per cell in the original structure, $z_c = 2(N+N_c)/N_c$, hence $N_c/N \leq 1/5$.

The opposite bound is obtained as follows. The highest packing density of identical smooth and rigid ellipsoids is achieved within a narrow range of aspect ratios where $\bar{z} = 14$.[15] Polydispersity is expected to reduce $\bar{z}$. This is supported numerically[16,17] and experimentally.[18] Therefore, we get a low bound by setting $z_c = 14$, $N_c/N \geq 1/6$. Therefore, the mean number of grains surrounding a cell is between 20 and 24. Combining the bounds with relation (6), we get $27/5 \leq N_{dof}/N \leq 11/2$ and the phase space is then $N_{dof} = (5.45 \pm 0.05)N$-dimensional. Thus, the fraction of the quadrons needed to span the phase space is narrowly bounded between 9/20 and 11/24. Choosing these DOF to be uniformly distributed in space, reduces the correlations between them and makes the ideal quadron gas a better approximation to compute the partition function and volume-based structural properties.

3. Calculations of other structural properties

Not all structural properties are convenient to compute with the quadrons as the DOF. An important example is the mean throat size, which is directly relevant to the permeability to fluid flow. The throat areas are difficult to express in terms of quadron volumes, but can be easily eritten in terms of the edge vectors $\vec{r}$. From the considerations above, the number of DOF per throat is

$$\frac{9}{2} \leq \frac{N_{dof}}{N_f} = \frac{3(2 - N_c/N)}{1 + N_c/N} \leq \frac{33}{7} \tag{7}$$

and the mean number of edge vectors around a face is

$$5 \leq \frac{6N}{N_f} = \frac{6}{1 + N_c/N} \leq \frac{36}{7} \ . \tag{8}$$

The computation of effective throat sizes is as follows. A throat is a non-planar polygon made of n triangles. The effective area to flow of a throat between cells c and c', whose centroids are A and A', can be estimated by the polygon's projection onto a plane perpendicular to the vector $\vec{R}_{cc'}$ extending from A to A' (see figure 3). Letting the polygon corners be $\vec{\rho}_i'$,

$i = 0, 1, ..., n-1$, $\vec{r}_i = \vec{\rho}_i' - \vec{\rho}_{i-1}'$, $\vec{\rho}_i = \vec{r}_i \times \vec{R}_{cc'}$ and placing the origin at $\vec{\rho}_0'$, the area of the projected throat is

$$A_{throat} = \frac{1}{2} \sum_{i=1}^{n-2} \vec{\rho}_i \times \sum_{j=i+1}^{n-1} \vec{\rho}_j \ , \tag{9}$$

giving the effective throat size in terms of the edge vectors. The mean throat size is then

$$\langle A_{throat} \rangle = \frac{1}{ZN_f} \int \sum_{throats} A_{throat} e^{-\beta \mathcal{W}(\{\vec{r}\})} \mathcal{P}(\{\vec{r}\}) D\{\vec{r}\} \ . \tag{10}$$

Computing similarly expectation values of higher powers of the sum in (9), we can construct the distribution of throat sizes to any required accuracy using techniques developed for the moment problem.

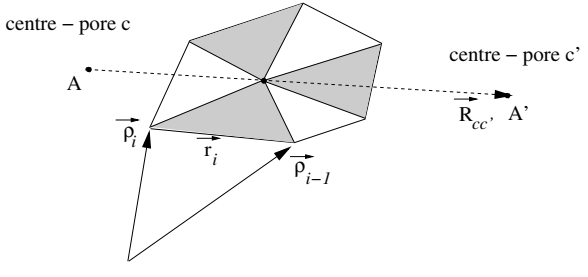

Fig. 3. A non-planar throat of the polyhedral structure is a non-planar throat. The vector $\vec{R}_{cc'}$ extends between the centroids of the cells c and c' which the throat connects. The effective area to flow is estimated as the projection of the polygon onto a plane perperndicular to $\vec{R}_{cc'}$.

The extension of this calculation for realistic throat size distribution, where the grain shape distribution is taken into consideration, is straightforward in the entropic formalism and will be described elsewhere. Other structural properties can be calculated similarly, e.g. the total surface area between the solid and the pore space, useful for estimating heat exchange.

4. The entropic formalism and mechanical stresses

The discussion about the statistics of granular systems in mechanical equilibrium is not complete without taking into consideration the mechanical

stresses that keep them in such states. The incorporation of stresses explicitly into the entropic formalism is a recent project in our group.[19] Of particular interest is stress transmission in isostatic materials. Why these idealized systems are useful to understanding general granular materials has been discussed in[20].[21] Stresses in planar systems are governed by

$$\partial_i \sigma_{ij} = g_j \quad (i,j = x,y) \quad ; \quad p_{xx}\sigma_{yy} + p_{yy}\sigma_{xx} = 2p_{xy}\sigma_{xy} \qquad (11)$$

with $\sigma_{xy} = \sigma_{yx}$ and $\vec{g}$ including external and body forces. The rightmost is a constitutive stress-structure relation, whose parameters p_{ij} characterize local structure. Their values were initially proposed empirically[22] and statistically[1] and eventually they have been derived from first principles. That derivation also highlighted their geometric interpretation on the grain level.[11] Equations (11) can be solved under simplifying assumptions[208] and they have been analysed rigorously recently.[23] All analyses confirm that localized source loads give rise in such media to force chains, in agreement with experiments[24] and simulations.[25] Here, I discuss the relations between these solutions and the entropic formalism.

The statistical and pure mechanical descriptions have developed largely independently, but they must be related. Measurements of contact force magnitude with exponential-tailed distributions led to statistical-mechanical based explanations that are independent of the solutions of (11)[2627].[28] Disregarding these solutions necessitated introduction of assumptions that weakened the models and led to much controversy.

This point can be illustrated in jamming of slowly sheared granular systems. The microstructure changes continuously in response to forces until the systems jams. We can now solve for the stress field in the jammed state, but it is the very stress solution which affected the structural characteristics. Thus, a full statistical mechanical description must include both the structural information and the boundary loading.

It is important to recall here two important differences between granular and thermal systems. Measurements in the latter are normally done on time scales that allow the system sufficient time to explore a sufficiently large number of states to render the data typical. Granular systems are in principle quenched in a given state, especially for stress measurements. The only statistics involved here could be through ensembles of systems. Another significant difference is that eqs. (11) are hyperbolic, which is the reason for the chain solutions. This means that fluctuations in boundary force loads can be felt far from the load source. For example, consider a granular material pressed within a container by a flat plate of area S with a

force F. Since the boundary of a granular pack is never flat then the plate presses on protruding grains differently than on their neighbours. These locally elevated forces act as localized load sources and give rise to chains. If the typical distance between such sources along the boundary is larger than the scale of resolution, or interest, then the particular distribution of chains is more significant than the mean pressure F/S. This suggests that: (i) care should be taken in the specification of the boundary loads and (ii) that one cannot ignore these fluctuations in the analysis of the statistics.
To address this issue we expand the phase space of DOF to include an ensemble of all the possible loads[19].[28] Consider an ensemble of all possible systems in mechanical equilibrium with given volume V and total boundary stress $\overline{\overline{\Pi}}$. Divide this ensembles into two sub-ensembles. One, the Π-ensemble, consists of all possible configurations of the particles that occupy a given volume V under a boundary loading of a given spatial distribution of force loads on the boundary. The other sub-ensemble, the V-ensemble, consists of all the possible realizations of boundary forces that add up to the boundary stress $\overline{\overline{\Pi}}$, such that the particular configuration of particles is kept fixed. Note that these are in fact all the stresses that are confined to within the so-called yield surface for this configuration.
The partition function can now be written as

$$Z = \int e^{-\mathcal{W}(\{q\},\{f\})/X_0 - \mathcal{F}(\{q\},\{f\})/(VX_{ij})} \Theta\left(\{q\},\{f\}\right) D\{q\} D\{f\} \ , \quad (12)$$

where $\{f\}$ are the DOF describing the boundary loads, e.g. by the forces on every boundary grain, $\mathcal{F}$ is the force moment (from which stresses are defined) and the function Θ is a product of δ-functions requiring both that the particles are in contact and that Newton's equations are satisfied. The variable X_0 is the compactivity, previously denoted by X, and X_{ij} are the components of a tensorial analogue of temperature defined via derivatives of the entropy S with respect to the boundary stresses

$$X_{ij} = \partial S / \partial \Pi_{ij} \ . \quad (13)$$

The tensor X_{ij} has been named angoricity.[28] The use of this formalism is currently explored in our group. In particular, we are looking into developing a Boltzmann equation, taking into consideration both the tensorial structural description and the newly discovered stress solutions into consideration.

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