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STRUCTURAL CHARACTERIZATION OF POROUS AND GRANULAR MATERIALS

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Summary. We review a recently-proposed method for quantifying internal structures of porous and granular materials in two and three dimensions. The method offers a systematic way to derive relations between the microstructure of such materials and their bulk properties. Preliminary results are presented for planar granular packs.

1 INTRODUCTION

The intricate pore structure of porous materials plays an essential role in determining their bulk behaviour. The key to understanding and predicting macroscopic properties of such materials, such as their transport properties, is by establishing structure-property relations – one of the holy grails in the field. The main problem has been that the large separation in length-scale between the pore size and relevant macroscopic behaviour hinders simple homogenisation techniques that start from the pore structure. As a result, the literature is littered with heuristic approaches, all with respective advantages and disadvantages.

To address this problem, a systematic method has been proposed to bridge between the scales[2−6]. The method comprises a programme that consists of several steps. The novelty lies in two key steps: quantification of the local structure, followed by a statistical characterisation of it, based on a statistical mechanical formalism. The latter allows us to compute physical properties on the mesoscale, which can be then used as objective input into network models. The method allows us to quantify global structural characteristics

in terms of local microstructural descriptors, and relate the structure to macroscopic physical properties, such as permeability, reactivity, solid-pore heat exchange, etc.

The quantification of the pore structure is carried out by dividing the pore space into elementary volumetric entities, called quadrons, whose shapes can be described by a shape tensor. A brief account of the construction of these entities is given in two and in three dimensions (2D and 3D). In 3D we focus, for illustration, on quadrivalent structures, where four edges meet at every vertex. The quadrons are used as 'quasi-particles', whose configurations can be treated entropically. Using then the powerful tools of conventional statistical mechanics, we can derive structural properties as expectation values over a certain partition function. The method is used initially on skeletons of porous materials. Nevertheless, the statistical mechanical approach allows us to extend the analysis to real 'thickened' structures.

We present preliminary results from the quantification of the microstructure of a planar dense granular pack. These include a distribution of the quadron areas and some conditional distributions related to it. In addition we consider the distribution of parameters that indicate the shape of the quadrons.

2 QUANTITATIVE DESCRIPTION OF THE PORE STRUCTURE

Given an image of a porous material, the first step is to reduce the solid phase into a skeletal representative. Such a skeleton forms a cellular structure – a collection of vertices (points) in space, with each vertex connected by edges, straight or curved, to adjacent vertices (e.g. the dotted lines of the 2D skeleton sketched in figure 1a). In this section, we review briefly the microstructure quantification method, on which our scheme is based. While our main interest is in 3D systems, it is insightful to describe the method first for planar systems.

2.1 Two dimensions

Consider a two dimensional skeleton, as in Fig. 1a. First, we determine the midpoints of the edges between vertices. We then join the midpoints by vectors $\mathbf{r}^{cv}$ that circulate around every vertex in the clockwise direction (forming polygons). Conversely, these vectors circulate around voids (cells) anticlockwise. We define the centroids of vertex and cell polygons as the arithmetic means of the positions of their corners. From the centroid of a vertex polygon, we extend vectors $\mathbf{R}^{cv}$ to the centroids of adjacent cells (see Fig. 1a). This results in two mutually reciprocal networks spanning the entire system – the $\mathbf{r}$-network and the $\mathbf{R}$-network.

Each $\mathbf{r}^{cv}$-$\mathbf{R}^{cv}$ pair forms a quadrilateral, of which they are the diagonals. The quadrilaterals, named *quadrons*[2, 3], offer a new way to characterize cellular (and granular, see below) structures. A key observation is that the quadrons tile the system. For brevity, we index the quadrons by q rather than cv. The quadron shape and geometry are quantified

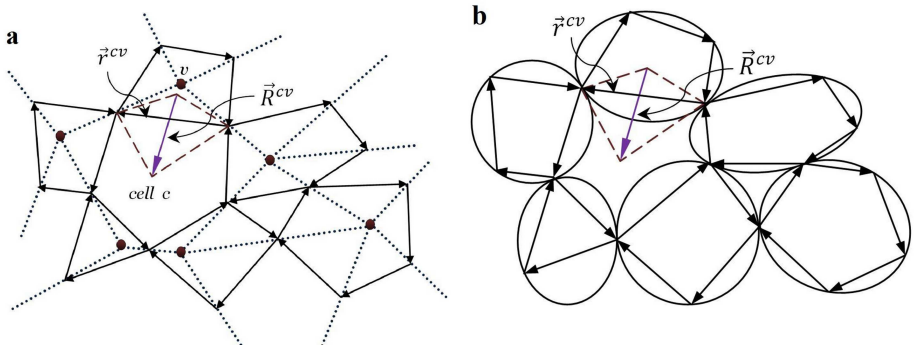

Figure 1: Structural characterization of planar systems: (a) A 2D skeleton of a porous material. Locate the midpoints on the edges that join the vertices. Join adjacent midpoints by vectors $\mathbf{r}^{cv}$, circulating clockwise around vertices and anticlockwise around cells. The centroids of vertex polygons and cell polygons are the mean positions of their respective corners. From a vertex centroid extend a vector $\mathbf{R}^{cv}$ to the centroid of an adjacent cell. Each pair $\mathbf{r}^{cv}$-$\mathbf{R}^{cv}$ forms a quadrilateral, of which they are the diagonals. The quadrilaterals, called *quadrons*, tile the plane. (b) The same construction can be used for granular packs: the edge midpoints map onto the inter-granular contact points and the $\mathbf{r}^{cv}$ vectors circulate around grains.

by a local shape tensor[2], formed by the outer product

$$C^q = (\hat{\varepsilon}\mathbf{r}^q) \otimes \mathbf{R}^q \tag{1}$$

where $\hat{\varepsilon} = \left(\begin{smallmatrix} 0 & 1 \\ -1 & 0 \end{smallmatrix}\right)$. Since the quadrons tile the plane, the volume of the system can be expressed as the sum of their areas, V^q:

$$\mathcal{W} = \sum_q V^q = \sum_q \frac{1}{2}\mathrm{Tr}C^q = \sum_q \frac{1}{2}\left(\mathbf{r}^q \times \mathbf{R}^q\right) \tag{2}$$

Being the elementary volumes makes the quadrons very useful for the statistical approach reviewed below (see Sec. 3).

While there is a number of ways to tessellate porous materials, the method described here has several advantages. One is that, unlike Voronoi tessellations, the quadrons are all quadrilaterals, making possible an unambiguous structural description in terms of the shape tensor. Another advantage, especially significant for granular systems (see below), is that the quadron construction is based on the physical connectivity of the structure - a feature that is lost by Voronoi-based methods. A third important advantage is that this method allows us to enumerate the degrees of freedom required to define the structure. This feature is significant for the construction of the statistical formalism described later. In 2D, the total number of quadrons coincides with the total number of degrees of freedom, allowing us to use quadrons as elementary 'quasi-particles'. The number of degrees of freedom is related to the number of the independent $\mathbf{r}^q$ vectors and, in 2D, it is equal to $N\bar{z}_v$, where N is the total number of vertices and z_v is the mean number of edges connected to a vertex (mean coordination number)[4, 5].

The same construction can be applied to granular packs[2, 4], where the vertices correspond to grains and edge midpoints are replaced by the grain contacts (see Fig. 1b). Joining adjacent contact points around a grain results in the same construction as for skeletons of porous media, with **r**-vectors circulating clockwise around grains and anticlockwise around voids. This mapping unifies the description of the structures of both types of systems.

2.2 Three dimensions

The rationale is the same as in 2D. First, one identifies the midpoints of the edges between vertices. Then, around each vertex, adjacent midpoints are joined by vectors to form a polyhedron, e.g. the tetrahedra as in Fig. 2a. The vectors circulate clockwise around a triangle when viewed from the vertex outward. The faces of the polyhedra are all triangular. The joining of edge midpoints also results in the formation of surfaces that enclose cells (pores). Such a surface comprises interconnected triangular faces, belonging to adjacent vertex polyhedra, and skew-polygonal faces, enclosed by these triangles (see figures 2 and 8 in ref. [6]). Each skew polygon is shared between two cells, constituting the 'throat' between them. We next construct quadron volume elements. The quadrons are non-convex octahedra, each containing local information on a cell, a vertex polyhedron and a polygonal throat. The construction of a quadron is illustrated in Figs. 2a-f for quadrivalent structures and explained in detail in the caption.

A 3D quadron is defined by three vectors: $\mathbf{r}^q$ – the edge shared by the triangular face and the skew polygon p; $\boldsymbol{\xi}^q$ – a vector extending from the centroid of the triangular face of the polyhedron to the centroid of polygon p; $\mathbf{R}^q$ – a vector extending from the centroid of the vertex polyhedron to the centroid of an adjacent cell. The quadron shape tensor is

$$C^q = (\boldsymbol{\xi}^q \times \mathbf{r}^q) \otimes \mathbf{R}^q \tag{3}$$

and the volume of a quadron is $V^q = \frac{1}{6}\mathrm{Tr}C^q = \frac{1}{6}(\boldsymbol{\xi}^q \times \mathbf{r}^q) \cdot \mathbf{R}^q$. By construction, the quadrons tessellate the space and their combined volume is the volume of the system. Unlike in 2D, there are more quadrons ($12N$, in quadrivalent structures) than degrees of freedom ($\sim 5.5N$) [5].

3 STATISTICAL MECHANICS OF GRANULAR ASSEMBLIES

It has been suggested[3] to extend the Edwards entropic formalism for granular packs[1] to cellular structures. The formalism, based on statistical mechanics, assumes that macroscopic cellular structures have a huge number of possible configurations (*microstates*). A configuration is defined by the positions of vertices, the connectivity, the shape of cells, etc. and it is specified by a set of variables, called the *degrees of freedom*.

The probability of a microstate depends on the volume occupied by the system in the corresponding configuration. It is expressed in terms of a Boltzmann-like factor, $e^{-\mathcal{W}/X}$,

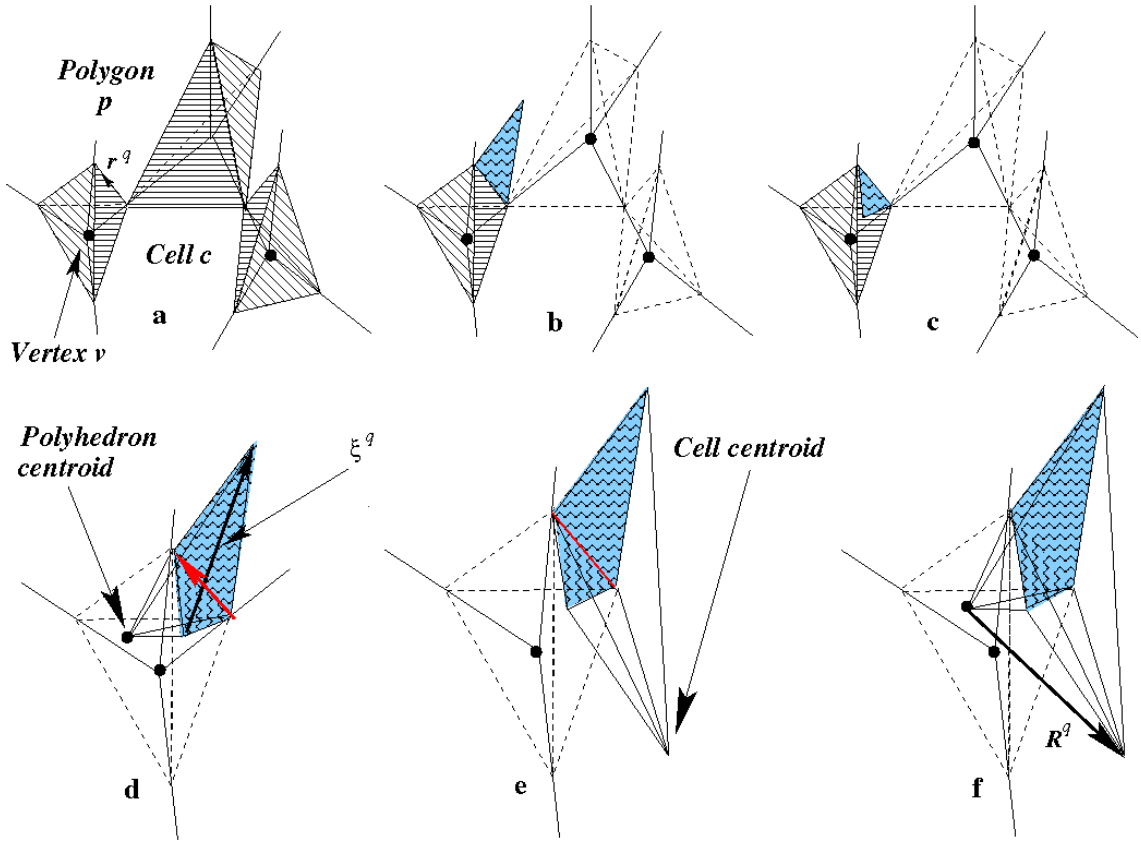

Figure 2: The construction of a *quadron*, e.g. in tetrahedral structures. (a) Three representative vertex tetrahedra, on the boundary of cell c. (b-c) Determine the centroids of the triangular face of the tetrahedron (shaded) and of the polygonal face p. Extend two lines from each of these to the tips of the edge shared by the triangle and the polygon, $\mathbf{r}^q$. This gives generically a skew (non-planar) quadrilateral. (d) Determine the centroid of the vertex tetrahedron and extend from it four lines to the corners of the skew quadrilateral of (c) to form a quasi-pyramid. (e) Determine the centroid of the cell and from it extend also four lines to the corners of the skew quadrilateral; this forms another quasi-pyramid that shares its base with the one constructed in (d). (f) The union of the two quasi-pyramids is a non-convex octahedron; this is the 3D quadron (figure curtesy of [3]).

where $\mathcal{W}$ is a volume function, giving the volume of the system, and X is a multiplier, analogous to the temperature in thermal systems, called *compactivity*. In granular packs, the compactivity is a measure of the porosity of the system.

A partition function is then defined,

$$Z = \int e^{-\mathcal{W}(\{\eta\})/X} \Theta(\{\eta\}) D\{\eta\} \tag{4}$$

where $\{\eta\}$ denotes the degrees of freedom and the integration is over all possible configurations within a given ensemble. $\mathcal{W}$ depends on the degrees of freedom $\{\eta\}$ and $\Theta(\{\eta\})$ rules out inadmissible configurations (e.g. which are not in mechanical equilibrium). The benefit of this approach is that it allows to calculate structural macroscopic properties as expectation values over *all* possible configurations. The expectation value of a property f is

$$\langle f \rangle = \frac{1}{Z} \int f(\{\eta\}) e^{-\mathcal{W}(\{\eta\})/X} \Theta(\{\eta\}) D\{\eta\} \tag{5}$$

For example, $\langle f \rangle$ could be the 'throat' mean size, its mean size fluctuations and other structural quantities which are important to compute local permeability and construct equivalent networks. It could be the total polyhedral surface area, which is important to estimate reactivity, catalysis, solid-pore heat exchange and other properties.

To use this approach, one needs to have a useful form of $\mathcal{W}$. The method described in Sec. 2 provides it, $\mathcal{W} = \sum_q V^q$, with $\{\eta\}$ being (a subset of) the vectors $\mathbf{r}^q$. Then the partition function becomes

$$Z = \int e^{-\sum_q V^q/X} \Theta(\{\mathbf{r}^q\}) \prod_{q=1, i=x,y,z}^{N_{dof}} \{dr_i^q\} \tag{6}$$

where N_{dof} is the number of degrees of freedom. Since, in 2D, the number of quadrons coincides with the number of degrees of freedom we can use their volumes as degrees of freedom. Using an 'ideal quadron gas' approximation[2] allows us to evaluate the partition function:

$$Z = \left(\int g(V^q) e^{-V^q/X} dV^q \right)^{N_q} \tag{7}$$

Here, $g(V^q)$ is the density of states – the frequency of states where a quadron's volume is in the interval $(V^q, V^q + dV^q)$ and N_q is the number of quadrons.

4 A DENSE PLANAR PACK

To test the method, illustrate some of its uses and provide insight into 3D structures, we first analyse a 2D system. Already the quantification of the pore structure is beneficial for characterizing porous materials and comparing between different types of structures. However, more significantly, the combination of the quantitative structural description and the statistical mechanical approach provides a way to derive relations between the pore structure and bulk physical properties of porous and granular materials[8].

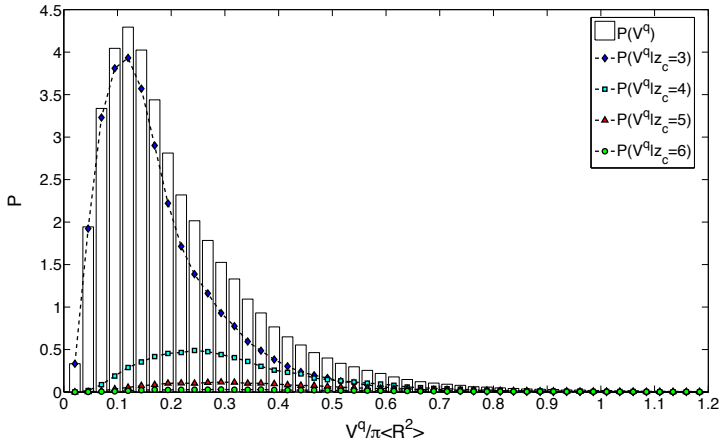

Figure 3: Quadron area distribution in a 2D dense granular pack (bars) and conditional distributions (superimposed curves). Here, $\langle R^2 \rangle$ is the average grain radius, and z_c is the cell (void) order.

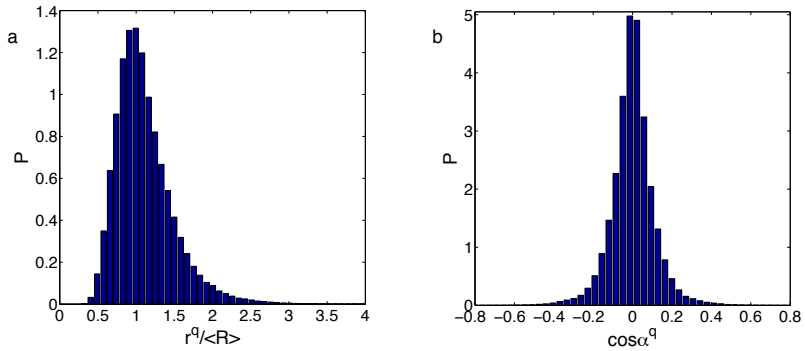

Figure 4: Additional distributions: magnitudes of the $\mathbf{r}^q$ vectors and the cosine of α^q – the angle between $\mathbf{r}^q$ and $\mathbf{R}^q$.

Here we report preliminary results on the distributions of the various variables related to the quadrons in dense 2D granular packs. The grains are polydisperse discs and the

pack is made very dense – over 80% of the voids have only 3 grains around them ($z_c = 3$). We have studied both the total distribution of quadron areas (bars in Fig. 3) and the conditional area distributions, given that a quadron belongs to a cell of z_c sides (superimposed curves in Fig. 3). The latter is motivated by the results of Frenkel *et al* [4] that these conditional distributions are independent of pack preparation, while the total distribution is not. Unlike Frenkel *et al*, our total distribution has no shoulders, which is a result of the location of the peaks of the conditional distributions for $z_c > 3$. This already shows a significant difference between the packs studied there and the one studied here.

We have also studied the magnitudes of the vectors $\mathbf{r}^q$ and the angles α^q between $\mathbf{r}^q$-$\mathbf{R}^q$ pairs (Fig. 4). As expected[7], the distribution of α^q is narrowly and roughly symmetrically peaked around $\pi/2$. We are currently extending the above analysis to a family of 3D skeletal structures.

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