Methods for describing structure of novel porous materials: a review

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Abstract. The physical and mechanical properties of heterogeneous materials are mainly determined by their structure. Due to the wide capabilities of modern technologies for the formation of complex multilevel pore structure of ceramics and other materials, the ability of modern methods to describe and characterize such a structure completely is of particular interest. Traditionally, the pore structure is characterized by a large number of parameters such as porosity, type and shape of pores, the fraction of cross-sectional area of channels, pore size distribution, etc. However, recently, at least three new quantities are often used to describe and measure the structure of various complex media: the Minkowski functionals, fabric tensors, and correlation functions. This review is aimed to consider all these three approaches and their capabilities for describing and measuring the peculiarities of the structure of porous materials.

1. Introduction

Due to the significant influence of the structure of the pore space on the strength and elastic properties of porous materials [1–7], as well as the wide capabilities of modern technologies for the formation of complex multilevel pore structure [8, 9], the ability of modern methods to describe and characterize such a structure completely is of particular interest. Traditionally, the structure of the pore space is characterized by the following parameters: porosity (volume fraction of all pores); its distribution in space; type of pores (open, closed, etc.); opening (the fraction of cross-sectional area of channels); shape and coefficient of pores tortuosity; pore size distribution; specific surface of pores; permeability and its distribution by filtration area [10]. Analysis of modern literature shows that at last decades three new approaches are also often used to describe and measure the structure of various complex media. The first approach is based on integral geometry and uses the Minkowski functionals and shapefinders. The second one uses so-called fabric tensors, which can be computed using both the geometric methods and the solid mechanics methods. The third approach is the most general and uses correlation functions. Below we consider all these three approaches and their capabilities for description and measuring the peculiarities of pore space structure of porous materials.

2. Minkowski functionals

In topology, the morphology of a three-dimensional structure can be completely determined by the following four quantities named Minkowski functionals (thereafter MFs) according to Hadwiger’s theorem [11]

\[ V_0 = \iiint dV; V_1 = \frac{1}{6} \iiint dS; V_2 = \frac{1}{6\pi} \iiint (\kappa_1 + \kappa_2) dS; V_3 = \frac{1}{4\pi} \iiint \kappa_1 \kappa_2 dS. \] (1)
where $\kappa_1$ and $\kappa_2$ are the principal curvatures of the structure surface. Note, that the coefficients before integrals in (1) depends on the purpose of further use of the functionals values and could be normalized, for example, for getting Minkowski polynomials [12, 13]. The meanings of the first two functionals are very simple: $V_0$ is the volume; $V_1$ is proportional to the surface area of the structure. $V_2$ provides information about the shape and is proportional to the integral mean curvature; the meaning of $V_3$ is ambiguous (so-called Euler characteristic related to number of clusters minus number of tunnels plus number of cavities). MFs can be used to calculate such additional quantities, called “shapefinders”, as the “thickness” $T$, the “breadth” $B$ and the “length” $L$ of the structure [14]

$$T = \frac{V_0}{2V_1}; B = \frac{2V_1}{\pi V_2}; L = \frac{3V_3}{4V_2}. \tag{2}$$

In addition, two dimensionless shapefinders “planarity” $P$ and “filamentarity” $F$ are used [14]

$$P = \frac{B - T}{B + T}; F = \frac{L - B}{L + B}. \tag{3}$$

Many features of a 3D structure can be analysed using a plot of the filamentarity versus planarity. For example, the simplest structures are characterized by the following values: line — $P = 0$, $F = 1$; plane — $P = 1$, $F = 0$; sphere — $P = F = 0$.

Using a scanner or tomography, any structure can be represented as a grid of pixels or voxels. Results of the computer simulations are also obtained on grids, including uniform ones. Then one can use the Adler’s algorithm to compute MFs in terms of such values as the number of grid nodes within the structure $n_0$; the number of edges $n_1$; the number of faces $n_2$; the number of cubic cells $n_3$; the total number of grid nodes $N$:

$$V_0 = n_0; V_1 = \frac{2(n_1 - 3n_2)}{9N}; V_2 = \frac{2(n_1 - 2n_2 + 3n_3)}{9N^2}; V_3 = \frac{n_0 - n_1 + n_2 - n_3}{N^3}. \tag{4}$$

In [12] the authors point out the importance of a morphological characterization of patterns in statistical physics. They illustrate the integral geometric approach to stochastic geometries by applying morphological measures to such diverse topics as percolation, complex fluids, and the large-scale galaxy distribution in the Universe. In particular, porous media may be generated by overlapping holes of arbitrary shape distributed uniformly in space. The percolation threshold of such porous media can be estimated accurately in terms of the morphology of the distributed pores. They also stress out that morphological measures are a novel method for the description of complex spatial structures aiming for relevant order parameters and structure information complement to correlation functions. Typical applications address Turing patterns in chemical reaction-diffusion systems, homogeneous phases evolving during spinodal decomposition, and the distribution of galaxies and clusters of galaxies in the Universe as a prominent example of a point process in nature.

In [13] the authors consider the effects of distortions (drift, noise, and blurring) on the morphological properties of complex random models, representative of a wide range of structure. Such distortions arise experimentally in imaging techniques due to diffraction, absorption and sample drift. The authors show how critically these distortions affect image quality as measured by the MFs.

In review [14] the authors give sufficient motivation for employing the Minkowski functionals in cosmology, they present a summary of the progress made in the direction of using the MFs to quantify the large scale structure by studying the geometry and topology of the superclusters and voids. Specifically, they stress the discriminatory power of MFs and of the derived morphological statistics, the shapefinders. Shapefinders are specifically important to study the shapes and sizes of the superclusters and voids. Several successes of shapefinders are highlighted there.

One of the important applications of using MFs to analyse complex structure belongs to computational fluid dynamics. For example, in [15] the authors consider an approach for studying the results of direct numerical simulation of large eddy simulations of multi-species turbulent mixing under high-pressure conditions.
Several metrics are used to understand the modelling results. First, a statistical analysis of the simulation results database for large-scale flow structures was performed to provide a metric for probing the accuracy of the proposed models as the flow fields obtained from accurate simulations should contain structures of morphology statistically similar to those observed in the filtered-and-coarsened simulations fields. To characterize the morphology of the large-scale structures, the Minkowski functionals of the iso-surfaces were evaluated for two different fields: the second-invariant of the rate of deformation tensor and the irreversible entropy production rate.

In [16] so-called anisotropic Minkowski functionals (AMFs) are used to capture local anisotropy while evaluating topological properties of the underlying grey-level structures. The authors evaluate the ability of this approach to characterize local structure properties of trabecular bone micro-architecture in ex vivo proximal femur specimens, as visualized on multidetector CT, for purposes of biomechanical bone strength prediction.

By virtue of their defining property of rotation-invariance, Minkowski functionals are not explicitly sensitive to directional and anisotropic features of morphology. This lack motivates the generalization to tensorial quantities, called Minkowski tensors. In [17] the authors provide a simple overview of the definition, properties and interpretation of Minkowski tensors, as well as advanced applications of these tensors to local anisotropy analysis of simple numerical models, to real-world data sets from scanning force microscopy of co-polymer films, X-ray tomography of granular matter and open-cell solid foams, and to defect detection in molecular dynamics simulations of metallic systems [18, 19].

It has to be noted, that Minkowski tensors can be also considered as a kind of fabric tensors, which are described in the next section. Good theoretical description of Minkowski functionals, their applications, as well as free software, are available online at https://morphometry.org/.

3. Fabric tensors
In modern scientific literature, the concept of fabric tensor is widely used to describe the structural features of various materials [20]. Apparently, it was initially used to describe the structure of geological media [21], then in medicine to study the structure of bone tissue [22–24], and, finally, in materials science for composites [17, 25]. Generally speaking, fabric tensors are understood as various tensor values that somehow characterize the structural sensitivity of a material. Fabric tensors aim at modelling through tensors both anisotropy and orientation of a material with respect to another one. These tensors can be seen as semi-global measurements since they are computed in relatively large neighbourhoods, which are assumed quasi-homogeneous. Therefore, in the review [20], the methods of the fabric tensor computation are classified into mechanics-based and morphology-based.

In its turn, mechanics-based methods can use the approach of solid mechanics; in this case, the simplest fabric tensor is the stiffness tensor. The second group of mechanics-based methods uses the wave propagation approach. Assuming poroelastic behaviour, it has been shown that wave propagation in trabecular bone, for example, can be characterized through the acoustic tensor, the solid-fluid interaction tensor, and the intrinsic permeability tensor, which describe the elastic and viscous effects in the media [24].

Morphology-based methods have two advantages compared to the mechanics-based methods. First, they are largely less computationally expensive than those obtained from mechanical simulations. Second, unlike methods based on mechanics, the resulting fabric tensors are not dependent on the boundary conditions applied during the simulations, homogenization schemes and/or general design of the simulations. However, as a counterpart, it is necessary to relate these fabric tensors with mechanical properties of the material, especially, elasticity. According to [20], a summary of the morphology-based methods is presented in Table 1.

| Table 1. Summary of morphology-based methods to compute fabric tensors. |
It is important to remark that fabric tensors are not global measurements. Thus, it is possible to obtain fields of fabric tensors where tensors are computed locally with respect to a neighbourhood. However, large neighbourhoods are usually used, since regions of interest are usually assumed homogeneous. This imposes the problem of determining the appropriate size of neighbourhoods.

4. Correlation functions

In [40], it is noted that the total amount of information contained in the Minkowski functionals is much less than is necessary to describe even a relatively simple structure. At the same time, there is a method that allows one to quantitatively describe the internal structure of an object, and it is based on the calculation of the so-called correlation functions [41–44].

Each correlation function describes the probability of a certain image configuration, for example, that the points at the ends of an arbitrary segment lying on the image being studied are in the same phase. The most complete description of the correlation functions is presented in the book [42]. The simplest type of correlation function (n-point correlation function) shows the probability of finding n points in the same phase. The value of the one-point correlation function is equal to the volume fraction of the binary fraction (for example, porosity). The two-point correlation function is defined as the probability of simultaneously landing points x1 and x2 in the same phase (pores or solid phase of a porous material) and is the most studied function for describing random media.

Concerning heterogeneous materials, any effective properties, $K_e$, is defined by a linear relationship between an average of a generalized local flux $F$ and an average of a generalized local (or applied) intensity $G$, i.e.,

$$F \propto K_e \cdot G$$  \hspace{1cm} (5)

As it is shown in [42], there are a variety of different correlation functions that naturally arise when the averaging process involved in relation (5) is rigorously carried out. Roughly speaking, the averaging process results in integrals in which the relevant local fields are weighted with the n-point correlation functions. More precisely, the averages are functionals of the n-point correlation functions.

In [40], it is also noted that for describing and restoring heterogeneous media there are not enough two-point correlation functions and under the prevailing conditions the most correct way of improving
the accuracy of structure description could be based on using additional low-order functions \((n \leq 2)\). Each of them represents the probability that the position of the endpoints of a segment or a segment itself must satisfy certain conditions. The following such functions have been proposed so far:

- cluster function (the segment ends are inside one cluster) [45];
- linear path function (the whole segment is in one phase) [46];
- chord length function [47];
- various functions of surfaces, for example surface-void and surface-surface functions [48];
- pore-size function [42].

At present, it is unknown which set of correlation functions is universal and sufficient for an accurate description of the structure and its properties for each specific case. Nevertheless, it is possible to increase the amount of information about the structure provided by the set of correlation functions by increasing their types and quantities. Correlation functions are a potential way to describe any structure because they allow correct solving the inverse problem and reconstructing the structure by the values of the complete set of correlation functions [40].

It is important that the correlation functions allow us to estimate how much information they can provide about a given structure. Such an estimate can be made by studying the parameters of the reconstruction algorithm and the number of confluent states when the same set of correlation functions corresponds to different structures [42, 43].

5. Conclusions

Review of the modern scientific literature shows that for a complete description of the complex structure the most powerful and mathematically correct are the use of Minkowski tensors and correlation functions. Fabric tensors are often actually the results that could be got after the structure analysis (at least for mechanics-based methods). The main advantage of the use of Minkowski functionals is that the corresponding free software is available with examples of its application. As a disadvantage of the use of correlation functions, we consider that their methods are based on random algorithms that seem to be very consuming in terms of computational time.

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References

[1] Konovalenko Ig S, et al 2009 Tech. Phys. 54 758–61
[2] Smolin A Yu, et al 2014 Eng. Fract. Mech. 130 53–64.
[3] Kalatur E, Buyakova S, Kulkov S and Narikovich A 2014 AIP Conf. Proc. 1623 225–8
[4] Smolin I Yu, et al S 2016 Proc. Struct. Integr. 2 3353–60
[5] Grigor’ev M V, et al 2017 Tech. Phys. Lett. 43 723–6
[6] Kulkov S N, et al 2015 Epitoanyag-JSBCM 67 155–8
[7] Grigoriev M V, et al 2018 Epitoanyag-JSBCM 70 18–22
[8] Zhukov I, Buyakova S P and Kulkov S S 2016 Epitoanyag-JSBCM 68 74–9
[9] Kulbakin D E, et al 2019 IOP Conf. Ser.: Mater. Sci. Eng. 511 012006
[10] Rouquerol J, et al 1994 Pure Appl. Chem. 66 1739–58
[11] Klain D A and Rota G-C 1997 Introduction to geometric probability (Cambridge University Press, Cambridge)
[12] Mecke K 1998 Int. J. Modern Phys. B 12 861–99
[13] Arns C H, Knackstedt M A and K Mecke 2010 J. of Microscopy 240 181–96
[14] Sheth V and Sahni V 2005 Current Science 88 1101–16
[15] Borghesi G and Bellan J 2015 Phys. Fluids 27 035117
[16] Nagarajan M B, De T, Lochmüller E-M, Eckstein F and Wismüller A 2014 Using anisotropic 3D
Minkowski functionals for trabecular bone characterization and biomechanical strength prediction in proximal femur specimens *Medical Imaging 2014: Biomedical Applications in Molecular, Structural, and Functional Imaging Proc. SPIE 9038* ed R C Molthen, J B Weaver (SPIE Medical Imaging, San Diego, CA) 9038:20

[17] Schröder-Turk G E, et al 2011 *Adv. Mater.* 23 2535–53
[18] Golovnev I F, Golovneva E I and Fomin V M 2008 *Phys. Mesomech.* 11 19–24
[19] Golovnev I F, et al 2015 *Phys. Mesomech.* 18 179–186
[20] Moreno R, et al 2014 Techniques for computing fabric tensors: a review *Visualization and processing of tensors and higher order descriptors for multi-valued data, mathematics and visualization* ed C-F Westin, et al (Springer-Verlag, Berlin) 271–92
[21] Launée P and Robin P Y F 1996 *Tectonophysics* 267 91–119
[22] Tabor Z and Rokita E 2007 *Bone* 40 966–72
[23] Varga P and Zysset P K 2009 *Med. Image. Anal.* 13 530–41
[24] Cowin S C and Cardoso L 2011 *Biomech. Model Mechanobiol.* 10 39–65
[25] Voyiadjis G Z and Kattan P I 2006 *Advances in Damage Mechanics: Metals and Metal Matrix Composites with an Introduction to Fabric Tensors* (Elsevier, Oxford)
[26] Moreno R, Borgia M and Smedby Ö 2012 *Med. Phys.* 39 4599–612
[27] Odgaard A 1997 *Bone* 20 315–28
[28] Xu Z, Saha P K and Dasgupta S 2012 *Comput. Vis. Image. Underst.* 116 1060–75
[29] Vasilč B, Rajapakse C S and Wehrli F W 2009 *Med. Phys.* 36 3280–91
[30] Majumdar S, et al 1999 *Med. Phys.* 26 1330–40
[31] Podsiadlo P, Dahl L, Englund M, Lohmander L S and Stachowiak G W 2008 *Osteoarthr. Cartil.* 16 323–9
[32] Wolski M, Podsiadlo P, Stachowiak G, Lohmander L and Englund M 2010 *Osteoarthr. Cartil.* 18 684–90
[33] Geraets W G M, et al 2008 *J. Biomech.* 41 2206–10
[34] Wald M J, Vasilč B, Saha P K and Wehrli F W 2007 *Med. Phys.* 34 1110–20
[35] Guggenbuhl P, Chappard D, Garreau M, Bansard J Y, Chales G and Rolland Y 2008 *Eur. J. Radiol.* 67 514–20
[36] Capuani S, Rossi C, Alesiani M and Maraviglia B 2005 *Solid State Nucl. Magn. Reson.* 28 266–72
[37] Graner F, Dollet B, Raufaste C and Marmottant P 2008 *Eur. Phys. J. E: Soft Matter Biol. Phys.* 25 349–69
[38] Kinney J H, Stöken J S, Smith T, Ryaby J T and Lane N 2005 *Bone* 36 193–201
[39] Brunet-Imbault B, Lemineur G, Chappard C, Harba R and Benhamou C L 2005 *BMC Med. Imaging* 5 4
[40] Karsanina M V 2016 *Modeling and reconstruction of structure and properties of porous media using correlation functions* PhD thesis (Institute of Geosphere Dynamics of Russian Academy of Sciences, Moscow) [in Russian]
[41] Torquato S 1991 *Appl. Mech. Rev.* 44 37–76
[42] Torquato S 2002 *Random Heterogeneous Materials: Microstructure and Macroscopic Properties* (Springer-Verlag, New York)
[43] Gommes C J, Jiao Y and Torquato S 2012 *Phys. Rev. E Stat. Nonlin. Soft Matter Phys.* 85 051140
[44] Gommes C J, Jiao Y and Torquato S 2012 *Phys. Rev. Lett.* 108 080601
[45] Torquato S, Beasley J D and Chiew Y C 1988 *J. Chem. Phys.* 88 6540
[46] Lu B and Torquato S 1992 *Phys. Rev. A.* 45 922
[47] Torquato S and Lu B 1993 *Phys. Rev. E.* 47 2950
[48] Jiao Y, Stillinge F H r, Torquato S 2007 *Phys. Rev. E.* 76 031110