On the significance of the microstructure to estimating of macroscopic properties of consolidated solids

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- Macroscopic and microscopic parameters of multiphase solids
- Methods of characterisation of microstructure
- Prediction of macroscopic properties

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Introduction – significance of microstructure

\[ \sigma_e = \phi_1 \sigma_1 + \phi_2 \sigma_2 \]

\[ \sigma_e = (\phi_1/\sigma_1 + \phi_2/\sigma_2)^{-1} \]

Example - effective electrical conductivity, \( \sigma_e \), of a two-phase material consisting of alternating slabs of phases with conductivities \( \sigma_1 \) and \( \sigma_2 \). The applied field is oriented parallel (left) and perpendicular (right) to the slabs. The volume fractions are the same: \( \phi_1 = 17/24 \) a \( \phi_2 = 7/24 \).
Properties of multiphase media

Basic property – heterogeneity if the objects, such as particles, pores, etc., are considered. Microstructural parameters are those properties that are completely determined by the microstructure of the medium and do not depend on any other property.

1. Macroscopic properties (≈ average properties of a large sample): volume fractions, specific phase interface area, formation resistivity factor, effective electrical/thermal conductivity, effective stiffness tensor, and reduced breakthrough capillary pressure.

2. Microscopic properties: geometry and topology of regions constituting the medium.
Macroscopic (statistical) homogeneity and heterogeneity

- A sample of a medium forms a macroscopic system if its repeated division into two halves and random selection of one half yields a smooth parameter (conductivity, volume fraction, etc.) variation as a function of the sample volume.

- As the sample becomes very small, the parameter is taken over a small number of the objects of interest and, hence, it will fluctuate with the sample size.

- The effect of object-scale heterogeneity on the macroscopic parameters is different. For instance, the permeability is more sensitive than the volume fraction.
Examples of multiphase media

Image of a 2D cut through a porous medium. The pores are dark, while the solid matrix is light.
Examples of multiphase media

Image of a 2D cut through a mixed-matrix membrane. The silicalite particles are light, while the polymer matrix is dark.
Mercury porosimetry and importance of microstructure

Primary data (left) and data processed using the common way (right)
Mercury porosimetry and importance of microstructure

Meniscus in a conical capillary (shape of truncated right circular cone)

The pressure difference between the non-wetting phase and the wetting phase is defined as the capillary pressure

\[ P_c = |P' - P''| = 2\gamma a^{-1} |\cos(\theta + \omega)|. \]

The magnitude of the angle \( \theta + \omega \) determines the sign of curvature of the meniscus. If \( \theta + \omega > \pi/2 \), \( P' - P'' < 0 \). \( \theta + \omega \approx 1.0472 < \pi/2 \) in the figure.
Mercury porosimetry and importance of microstructure

Three right circular cylinders of the same height, $h$: $V_i = \pi r_i^2 h$. $\theta = 40^\circ$.

Saturation as a function of external pressure, $P_e$. $r_1 = 2$, $r_2 = 4$ a $r_3 = 1$. 
Reconstructing the microstructure

- Serial sectioning (invasive), modern variants available – nanoscale serial sectioning using a dual-beam instrument (FIB-SEM).
- X-ray computed micro-tomography (non-invasive).
- High-resolution transmission electron microscopy with tomographic extension.
- Laser confocal microscopy (non-invasive).
- Process-based methods (model processes of formation of media).
- Stochastic reconstruction – different approaches based on thresholding Gaussian random fields or simulated annealing (SA). (invasive, imaging 2D cuts, random position).
- Boolean methods: packing of overlapping particles.
Nanoscale serial sectioning: FIB-SEM

The analysed volume can be as large as $30 \times 30 \times 15 \, \mu m^3$. The best achievable z-spacing is about 10 nm.
X-ray computed micro-tomography

- Synchrotron radiation facilities – imaging low-contrast specimens, fast acquisition.
- Desktop systems – low X-ray flux and longer data acquisition.
- The resolution is about 0.5 \( \mu \text{m} \) for common setups, but can reach 50–100 nm using scintillators and magnification optics.
- Monitoring structural dynamic processes.
Volume image processing

- Initial processing: cropping, alignment, correction of non-uniform illumination, etc.
- Spatial filtering: suppressing noise in the spatial or frequency domain. Rank filters. Advanced filters based on anisotropic non-linear diffusion

\[
\frac{\partial u}{\partial t} = \text{div}(G(\nabla u_\sigma \nabla u_\sigma^T) \cdot \nabla u)
\]

- Segmentation via the use of global or local properties. Global or local thresholding, watershed, indicator kriging, . . .
Smoothing raw images – edge enhancing diffusion

Left: 2D image selected from the volume image obtained using X-ray computed microtomography. Right: effect of the edge-enhancing diffusion filter
Particle packing created by sequential ballistic deposition. Left: circular discs with the log-normal distribution. Right: the same spheres.
Process-based methods: sintering

Sequential ballistic deposition of polydisperse spheres combined with sintering. Left: initial sphere packing. Right: packing after sintering.
Description of microstructure

Digitised two-phase medium: the indicator (phase) function, \( I^{(i)}(\mathbf{x}) \), for phase \( i \)

\[
I^{(i)}(\mathbf{x}) = \begin{cases} 
1, & \text{if } \mathbf{x} \text{ belongs to phase } i \\
0, & \text{otherwise} 
\end{cases}
\]

where \( \mathbf{x} \in \mathbb{V} \) is the position vector and \( \mathbb{V} \) is the convex region of space filled by the medium. Note that \( I^{(0)}(\mathbf{x}) + I^{(1)}(\mathbf{x}) = 1 \).

Discrete values of \( \mathbf{x} \) are determined by a simple cubic lattice of the size \( al_1 \times al_2 \times al_3 \) in the 3D medium \( (\mathbf{x} = (x_1, x_2, x_3)) \) and \( l_1, l_2, \) and \( l_3 \) are integers. The distance \( a \) between two adjacent lattice nodes corresponds to cubic voxel (3D) size.
3D replica of porous stain-less steel

A region of $160 \times 160 \times 160$ voxels is only shown. Phase interface is blue, pore orifices are yellow and the solid phase is transparent.
3D replica of mixed-matrix membrane

A region of $300 \times 300 \times 300$ voxels is only shown. Phase interface is green, cuts through silicalite-1 particles are red and the polyimide phase is transparent.
Statistical description of microstructure

- Note that $\langle \cdot \rangle$ stands for an ensemble average.

- $n$-point probability function, $S_n^{(i)}(x_1, \ldots x_n)$, for phase $i$, 
  \[ S_n^{(i)}(x_1, \ldots x_n) = \langle \prod_{j=1}^{n} I^{(i)}(x_j) \rangle, \]
  for $n = 2$, two-point probability function: 
  \[ S_2^{(i)}(x_1, x_2) = \langle I^{(i)}(x_1)I^{(i)}(x_2) \rangle, \]

- lineal-path function, $L^{(i)}(x_1, x_2)$, for phase $i$, 
  i.e., the probability that a line segment of length $u$ lies wholly in phase $i$ when randomly thrown into the sample,

- chord-length density function,

- two-point cluster function, $C_2^{(i)}(x_1, x_2)$, for phase $i$, 
  i.e., the probability of finding both ends of a line segment of length $u$ in the same cluster of phase $i$ when randomly thrown into the sample,

- surface correlation functions,

- pore-size distribution functions, etc.
Examples of microstructural descriptors

\[ R(u), \quad S_2 \]

\[ \tilde{L}^\nu, \quad \tilde{C}_2 \]

\[ \tilde{L}^s(u), \quad \tilde{S}_2 \]
Stochastic reconstruction: typical data acquisition

Three basic steps of data acquisition

• Impregnation of a porous material by a low-viscosity epoxy resin under vacuum and high pressure conditions.

• Cutting, grinding, and cross-section polishing of a hardened resin block.

• Polished sections imaged by means of a scanning electron microscope in the back-scattered electron mode (BSE). 40–100 images per sample.

Image processing

• BSE as “a chemical probe”: Areas where heavy elements prevail are light while areas where light elements are concentrated are dark.

• Each raw image is filtered (noise reduction) and segmented (binarised) into black and white pixels. The colours carry information on phases (the pore space or the solid matrix).
Stochastic reconstruction and tip enhanced Raman spectroscopy
Stochastic reconstruction and simulated annealing

Temperature schedule, \( \vartheta = f(\text{time}) \). Initial, intermediate and final stages of 2D reconstruction. Phase functions in windows of 160 × 256 pixels.
Transport phenomena simulated using 3D replicas

1. Steady viscous flow of an incompressible liquid: Stokes equations

\[ \mu \nabla^2 V(x) = \nabla P(x) \]
\[ \nabla \cdot V(x) = 0 \]

Data reduction results in effective permeability, \( \beta \), m\(^2\)

2. Diffusion: a random-walk algorithm that is based on a well-known functional relationship between the mean-squared displacement \( \langle \xi^2 \rangle \) of the walker and the time \( t \)

\[ D_e = \lim_{t \to \infty} \frac{\langle \xi^2 \rangle}{6t} = \lim_{t \to \infty} \frac{\langle (r_1(t) - r_1^0)^2 + (r_2(t) - r_2^0)^2 + (r_3(t) - r_3^0)^2 \rangle}{6t} \]
Flow of incompressible fluid in a porous medium

Velocity field in a plane perpendicular to the direction of macroscopic flow.
Conclusions

- Advanced characterisation methods resolving objects of interest (e.g., particles, pores, etc.) and resulting in volume images of the media offer new opportunity to better understand many processes taking place in the medium.

- There is a possibility of predicting effective (macroscopic) properties from first principles.

- The mathematical models enable detailed modelling of various phenomena, e.g., multiphase flow in pore space.

- The models enable “natural” explanation of phenomena, such as the hysteresis loop observed in mercury porosimetry or Haines jumps inherently related to displacement of two immiscible fluids.

- Expensive apparatuses are needed.

- Computationally very intensive.
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