Available online at www.sciencedirect.com
ScienceDirect
Cement and Concrete Research 37 (2007) 351 – 359
Cement and Concrete Research

Toolbox for 3D imaging and modeling of porous media: Relationship with transport properties

P. Levitz

Laboratoire de Physique de la Matière condensée, Ecole Polytechnique-CNRS, 91128, Palaiseau, France

Received 5 October 2005; accepted 16 August 2006

Abstract

Porous media can be considered as interfacial systems where an internal surface partitions and fills the space in a complex way. Meaningful structural features appear on a length-scale where physical chemistry plays a central role either to impose a specific organisation on the material or to strongly modify the dynamics and the thermodynamics of the embedded fluids. A key issue is to understand how the geometrical and interfacial confinement affects numerous phenomena such as molecular diffusion, excitation relaxation, reaction kinetics, phase transitions, adsorption and capillary condensation. We will first review some experimental techniques able to image the 3D structure of disordered porous media. In the second part, we will analyse the geometrical and particularly some topological properties of a disordered porous material. We will discuss the interest and the limits of several strategies for obtaining 3D representations of various pore networks starting from an incomplete set of morphological characterisations. Finally, connection between geometry and diffusive transport will be presented, with emphasis on the application of pulsed gradient spin echo NMR technique as a tool for a multiscale analysis of transport in a confining geometry.

Keywords: Porous media; Morphology; Topology; 3D imaging; Small angle scattering; Diffusive transport; Pulse gradient spin echo NMR

1. Introduction

A mesoscopic divided matter and/or material (MDM) is an interfacial system where an internal surface partitions and fills the space in a complex way. MDM meaningful structural features appear on a length where physical chemistry plays a central role to impose a structure and a specific arrangement of constituent parts of the material (texture). The mesoscopic scale often coincides with the colloidal scale (submillimetric and lower). Pastes, slurries, cements, concretes, cokes, soil, catalysts, wood, paper coating, organised molecular systems, and ceramics are a few examples of MDM. Many of these materials can also be considered as disordered porous materials.

Looking at the interfacial properties of these media, especially the role of curvature, we can propose a preliminary textural classification. First, some materials are made of well-defined particles. In other words, we are dealing with a granular medium. In the case of clay pastes, each particle appears as a flat membrane at the atomic scale. These membranes can be strongly crumpled as encountered for a coke microtexture. By elimination of interfacial boundaries we get a collection of distinctive individual particles such as spheres, ellipsoids, needles, or globular particles. Finally, the internal interface can be considered as a whole, multiconnected in space without borders which is archetypal of biphasic disordered porous media, exhibiting a more or less complex topology. Triply periodic minimal surfaces [1] encountered in oil–water, lipid, block copolymer and other amphiphilic systems, and templated nanostructured solid surfaces such as MCM48 [2], all belong to this class of MDM.

The degree of disorder is another way to classify MDM textures. A large class of MDM is relatively homogeneous with a defined disorder length-scale. It is then easy to find a representative elementary volume (REV), such that averages of physical properties are possible and meaningful. In the following, such matrix will be called "weakly disordered textures". On the other hand, several materials exhibit strong disorder and heterogeneity at different length-scales. In this case a REV cannot be defined and any averaging is length-scale sensitive. The fractal geometric [3,4] description provides a simple way to go from one to another length-scale. The associated geometrical

---

E-mail address: levitz@pmc.polytechnique.fr.

0008-8846/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.cemconres.2006.08.004

transformation is based on statistical length-scale invariance. A fractal object keeps the same statistical morphology on a magnification or a change of scale. Two interesting properties can be mentioned at this level. First, let us try to tile the fractal matrix with a collection of yardsticks having a typical size ε. The total number of yardsticks needed to cover the all object is proportional to ε^{-df}. Here d_f is the fractal dimension ranging between 0 and 3. Secondly, for a self-similar structure, the mass contained inside a box of size L evolves as L^{df}. Fractal geometry can be applied in numerous other cases. However, some hierarchical textures having specific organisation at different length-scales are still difficult to describe as a "whole".

A key issue is to understand how the geometrical and interfacial confinement affects numerous phenomena such as molecular diffusion, excitation relaxation, reaction kinetics, phase transitions, adsorption and capillary condensation [5,6]. This raises the challenge of describing the geometry of the pore network. Three levels of analysis are encountered in the literature. At the first level, apparently the most simple, the aim is to obtain a few numbers, which characterise the global properties of the porous material. One can first ask how much space the pore network occupies. One can introduce the porosity, ϕ, defined as the ratio of void (or pore) volume over total sample volume. A subtler question deals with the overall amount of interface per unit of volume (S_v). However, ϕ and S_v do not provide any clear information about the morphology of the pore network. One has to reach a second level of characterisation where questions are raised about average pore size mean curvature, pore shape, surface roughness, structural correlation between points belonging to the solid, the interface or the pore network. Finally, the last level concerns a topological analysis of the matrix [7,8], which is closely related to the long-range connectivity or percolation of pore network (Gauss curvature of the interface $\langle K \rangle$, deformation retract, genus of the interface). Several interesting properties should be analysed at this level such as the number of available paths linking two distinct points of the pore network, the metric distance between two points compared to their shortest (geodesic) distance and the important role of pore throats. It is clear that several terms are ill defined or ambiguous. This is for example the case for the average pore shape of a disordered pore network. It becomes evident that porous media *must be characterised in statistical terms*. One important goal is to handle correctly the pore structure at different length-scales in relation to the thermodynamics and molecular dynamics inside these confined and often disordered geometries.

In this paper, we first introduce the challenging problem of obtaining a reliable description of the MDM texture. In the second part, we discuss temporal and spatial properties of molecular confined dynamics inside porous materials and their potential connections with experiments such as pulse field gradients NMR.

2. Experimental tools

2.1. Some imaging techniques

Experimental imaging techniques play an important role in understanding the structure of mesoscopic disordered media and more particularly the geometrical organisation of porous materials. It is relatively "easy" to provide 2D images of the material at high resolution, using either transmission electron microscopy (TEM, resolution up to some Å) or scanning electron microscopy (SEM). One tedious way to get a 3D reconstruction is to perform serial sections as close as possible to each other (that is the major limiting factor) and piling them up. Such a protocol was used to analyse soil [9] (see Fig. 1). Generally, this difficult and tedious work cannot be performed at the same resolution (as high as possible) in the three spatial directions. However, a novel serial sectioning procedure for 3D analysis using a dual-beam FIB (focused ion beam) was recently proposed [10]. The acquired stack of images can be transformed directly into 3D data volume with a voxel resolution of 15 nm. Several other techniques to get 3D images of various materials are available. Among them, we can mention Magnetic Resonance Imaging (see Fig. 2 and [11,12]) or X-ray microtomography (see Fig. 3) which are generally non-invasive but with typical resolution not lower than 0.1 μm. Another interesting approach is the TEM tomography [13] already used to image biological materials at very high resolution. In the near future, optics of coherent X-rays will certainly provide new 3D imaging methods at higher resolution.

2.2. Structural correlation and small angle scattering techniques

Another alternative to probe the MDM morphology is to look at structural correlations [14,16]. The goal is to correlate the structural state (i.e. with reference to the solid matrix or to the internal interface) of two distinct points separated by a distance r. These structural correlations quantify how the 'memory' of an initial state is progressively lost when a point is moved away. Two-point correlation functions such as the bulk, the surface autocorrelation or the pore-surface correlation functions can be defined. They play a central role in different processes involving energy, excitation or molecular transport. Moreover, as shown in the seminal work of Doi [15,16], these three correlation functions are directly involved in an upper bound limit of the permeability. Clearly a statistical geometrical analysis of these two-point correlation functions is required. Debye et al. [17] performed one

Fig. 1. 3D reconstruction of the soil core by serial sectioning. The pixel resolution is 100 μm (adapted from [9,10]). The region of interest is 1 mm in dimension.