Transport in Porous Media **46:** 373–390, 2002.

Review on Scale Dependent Characterization of the Microstructure of Porous Media

R. HILFER
ICA-1, Universität Stuttgart, 70569 Stuttgart, Germany Institut für Physik, Universität Mainz, 55099 Mainz, Germany

Abstract. The paper discusses local porosity theory and its relation with other geometric characterization methods for porous media such as correlation functions and contact distributions. Special emphasis is placed on the charcterization of geometric observables through Hadwigers theorem in stochastic geometry. The four basic Minkowski functionals are introduced into local porosity theory, and for the first time a relationship is established between the Euler characteristic and the local percolation probabilities. Local porosity distributions and local percolation probabilities provide a scale dependent characterization of the microstructure of porous media that can be used in an effective medium approach to predict transport.

Key words: porous media, microstructure, geometrical characterization of porous media, structural properties, flow in porous media, transport in porous media micro-macro-transition.

1. Introduction

A crucial prerequisite for the prediction of transport parameters of porous media is a suitable characterization of the microstructure (Adler, 1992; Dullien, 1992; Sahimi, 1995; Hilfer, 1996). Despite a long history of scientific study the microstructure of porous media continues to be investigated in many areas of fundamental and applied research ranging from geophysics (Hearst and Nelson, 1985), hydrology (Marsily, 1986; Bear and Verruijt, 1987), petrophysics (Lake, 1989) and civil engineering (Ehlers, 1995; Diebels and Ehlers, 1996) to the materials science of composites (Crivelli-Visconti, 1998).

My primary objective in this article is to review briefly the application of local porosity theory, introduced in (Hilfer, 1991, 1992, 1996), as a method that provides a scale dependent geometric characterization of porous or heterogeneous media. A functional theorem of Hadwiger (Hadwiger, 1955, p. 39) emphasizes the importance of four set-theoretic functionals for the geometric characterization of porous media. In contrast herewith local porosity theory has emphasized geometric observables, that are not covered by Hadwigers theorem (Hilfer, 1993; Haslund *et al.*, 1994; Hilfer *et al.*, 1994). Other theories have stressed the importance of correlation functions (Torquato and Stell, 1982; Stell, 1985) or contact distributions (Levitz and Tchoubar, 1992; Muche and Stoyan, 1992; Stoyan *et al.*, 1995) for character-

ization purposes. Recently advances in computer and imaging technology have made three-dimensional microtomographic images more readily available. Exact microscopic solutions are thereby becoming possible and have recently been calculated (Biswal *et al.*, 1999; Widjajakusuma *et al.*, 1999a, b). Moreover, the availability of three-dimensional microstructures allows to test approximate theories and geometric models and to distinguish them quantitatively.

Distinguishing porous microstructures in a quantitative fashion is important for reliable predictions and it requires apt geometric observables. Examples of important geometric observables are porosity and specific internal surface area (Bear, 1972; Dullien, 1992). It is clear, however, that porosity and specific internal surface area alone are not sufficient to distinguish the infinite variety of porous microstructures.

Geometrical models for porous media may be roughly subdivided into the classical capillary tube and slit models (Dullien, 1992), grain models (Stoyan *et al.*, 1995), network models (Fatt, 1956; Bryant *et al.*, 1993), percolation models (Chatzis and Dullien, 1977; Sahimi, 1993), fractal models (Katz and Thompson, 1986; Roy and Tarafdar, 1997), stochastic reconstruction models (Quiblier, 1984; Adler, 1992) and diagenetic models (Roberts and Schwartz, 1985; Bakke and Øren, 1997). Little attention is usually paid to match the geometric characteristics of a model geometry to those of the experimental sample, as witnessed by the undiminished popularity of capillary tube models. Usually the matching of geometric observables is limited to the porosity alone. Recently the idea of stochastic reconstruction models has found renewed interest (Adler, 1992; Roberts, 1997; Yeong and Torquato, 1998). In stochastic reconstruction models one tries to match not only the porosity but also other geometric quantities such as specific internal surface, correlation functions, or linear and spherical contact distributions. As the number of matched quantities increases one expects that also the model approximates better the given sample. Matched models for sedimentary rocks have recently been subjected to a quantitative comparison with the experimentally obtained microstructures (Biswal *et al.*, 1999).

2. Geometrical Problems in Porous Media

A two-component porous sample $\mathbb{S} = \mathbb{P} \cup \mathbb{M}$ is defined as the union of two closed subsets $\mathbb{P} \subset \mathbb{R}^3$ and $\mathbb{M} \subset \mathbb{R}^3$ where $\mathbb{P}$ denotes the pore space (or component 1 in a heterogeneous medium) and $\mathbb{M}$ denotes the matrix space (or component 2). For simplicity only two-component media will be considered throughout this paper, but most concepts can be generalized to media with an arbitrary finite number of components. A particular pore space configuration may be described using the characteristic (or indicator) function $\chi_{\mathbb{P}}(\boldsymbol{r})$ of a set $\mathbb{P}$. It is defined for arbitrary sets $\mathbb{P}$ as

$$\chi_{\mathbb{P}}(\boldsymbol{r}) = \begin{cases} 1 & \text{for} \quad \boldsymbol{r} \in \mathbb{P} \\ 0 & \text{for} \quad \boldsymbol{r} \notin \mathbb{P}. \end{cases} \tag{1}$$

The geometrical problems in porous media arise because in practice the pore space configuration $\chi_{\mathbb{P}}(\boldsymbol{r})$ is usually not known in detail. On the other hand the solution of a physical boundary value problem would require detailed knowledge of the internal boundary, and hence of $\chi_{\mathbb{P}}(\boldsymbol{r})$.

While it is becoming feasible to digitize samples of several mm^3 with a resolution of a few μm this is not possible for larger samples. For this reason the true pore space $\mathbb{P}$ is often replaced by a geometric model $\widetilde{\mathbb{P}}$. One then solves the problem for the model geometry and hopes that its solution $\widetilde{u}$ obeys $\widetilde{u} \approx u$ in some sense. Such an approach requires quantitative methods for the comparison of $\mathbb{P}$ and the model $\widetilde{\mathbb{P}}$. This in turn raises the problem of finding generally applicable quantitative geometric characterization methods that allow to evaluate the accuracy of geometric models for porous microstructures. The problem of quantitative geometric characterization arises also when one asks which geometrical characteristics of the microsctructure $\mathbb{P}$ have the greatest influence on the properties of the solution u of a given boundary value problem.

Some authors introduce more than one geometrical model for one and the same microstructure when calculating different physical properties (e.g. diffusion and conduction). It should be clear that such models make it difficult to extract reliable physical or geometrical information.

3. Geometric Characterizations

3.1. GENERAL CONSIDERATIONS

A general geometric characterization of stochastic media should provide macroscopic geometric observables that allow to distinguish media with different microstructures quantitatively. In general, a stochastic medium is defined as a probability distribution on a space of geometries or configurations. Probability distributions and expectation values of geometric observables are candidates for a general geometric characterization.

A general geometric characterization should fulfill four criteria to be useful in applications. These four criteria were advanced in (Hilfer, 1996). Firstly, it must be well defined. This obvious requirement is sometimes violated. The so called 'pore-size distributions' measured in mercury porosimetry are not geometrical observables in the sense that they cannot be determined from knowledge of the geometry alone. Instead they are capillary pressure curves whose calculation involves physical quantities such as surface tension, viscosity or flooding history (Hilfer, 1996). Secondly, the geometric characterization should be directly accessible in experiments. The experiments should be independent of the quantities to be predicted. Thirdly, the numerical implementation should not require excessive amounts of data. This means that the amount of data should be manageable by contemporary data processing technology. Finally, a useful geometric characterization should be helpful in the exact or approximate theoretical calculations.

3.2. GEOMETRIC OBSERVABLES

Well defined geometric observables are the basis for the geometric characterization of porous media. A perennial problem in all applications is to identify those macroscopic geometric observables that are relevant for distinguishing between classes of microstructures. One is interested in those properties of the microstructure that influence the macroscopic physical behaviour. In general this depends on the details of the physical problem, but some general properties of the microstructure such as volume fraction or porosity are known to be relevant in many situations. Hadwigers theorem (Hadwiger, 1955) is an example of a mathematical result that helps to identify an important class of such general geometric properties of porous media. It will be seen later, however, that there exist important geometric properties that are not members of this class.

A geometric observable f is a mapping (functional) that assigns to each admissible pore space $\mathbb{P}$ a real number $f(\mathbb{P}) = f(\mathbb{P} \cap \mathbb{S})$ that can be calculated from $\mathbb{P}$ without solving a physical boundary value problem. A functional whose evaluation requires the solution of a physical boundary value problem will be called a physical observable.

Before discussing examples for geometric observables it is necessary to specify the admissible geometries $\mathbb{P}$. The set $\mathcal{R}$ of admissible $\mathbb{P}$ is defined as the set of all finite unions of compact convex sets (Hadwiger, 1955; Schneider and Weil, 1992; Schneider, 1993; Stoyan *et al.*, 1995). Because $\mathcal{R}$ is closed under unions and intersections it is called the convex ring. The choice of $\mathcal{R}$ is convenient for applications because digitized porous media can be considered as elements from $\mathcal{R}$ and because continuous observables defined for convex compact sets can be continued to all of $\mathcal{R}$. The set of all compact and convex subsets of $\mathbb{R}^d$ is denoted as $\mathcal{K}$. For subsequent discussions the Minkowski addition of two sets $\mathbb{A}, \mathbb{B} \subset \mathbb{R}^d$ is defined as

$$\mathbb{A} + \mathbb{B} = \{\boldsymbol{x} + \boldsymbol{y} \colon \boldsymbol{x} \in \mathbb{A}, \boldsymbol{y} \in \mathbb{B}\}. \tag{2}$$

Multiplication of $\mathbb{A}$ with a scalar is defined by $a\mathbb{A} = \{a\boldsymbol{x} \colon x \in \mathbb{A}\}$ for $a \in \mathbb{R}$.

Examples of geometric observables are the volume of $\mathbb{P}$ or the surface area of the internal $\partial\mathbb{P} = \partial\mathbb{M} = \mathbb{P} \cap \mathbb{M}$.[1] Let

$$V_d(\mathbb{K}) = \int_{\mathbb{R}^d} \chi_{\mathbb{P}}(\boldsymbol{r}) \mathrm{d}^d\boldsymbol{r}, \tag{3}$$

denote the d-dimensional Lebesgue volume of the compact convex set $\mathbb{K}$. The volume is hence a functional $V_d \colon \mathcal{K} \to \mathbb{R}$ on $\mathcal{K}$. An example of a compact convex

[1] The boundary $\partial\mathbb{G}$ of a set $\mathbb{G}$ is defined as the difference between the closure and the interior of $\mathbb{G}$ where the closure is the intersection of all closed sets containing $\mathbb{G}$ and the interior is the union of all open sets contained in $\mathbb{G}$.

set is the unit ball $\mathbb{B}^d = \{\boldsymbol{x} \in \mathbb{R}^d\colon |\boldsymbol{x}| \leqslant 1\} = \mathbb{B}^d(\mathbf{0}, 1)$ centered at the origin $\mathbf{0}$ whose volume is

$$\kappa_d = V_d(\mathbb{B}^d) = \frac{\pi^{d/2}}{\Gamma(1 + (d/2))}. \tag{4}$$

Other functionals on $\mathcal{K}$ can be constructed from the volume by virtue of the following fact. For every compact convex $\mathbb{K} \in \mathcal{K}$ and every $\varepsilon \geqslant 0$ there are numbers $V_j(\mathbb{K})$, $j = 0, \ldots, d$ depending only on $\mathbb{K}$ such that

$$V_d(\mathbb{K} + \varepsilon\mathbb{B}^d) = \sum_{j=0}^{d} V_j(\mathbb{K})\varepsilon^{d-j}\kappa_{d-j}, \tag{5}$$

is a polynomial in ε. This result is known as Steiners formula (Hadwiger, 1955; Stoyan *et al.*, 1995). The numbers $V_j(\mathbb{K})$, $j = 0 \ldots, d$ define functionals on $\mathcal{K}$ similar to the volume $V_d(\mathbb{K})$. The quantities

$$W_i(\mathbb{K}) = \frac{\kappa_i V_{d-i}(\mathbb{K})}{\binom{d}{i}}, \tag{6}$$

are called quermassintegrals (Schneider, 1993). From (5) one sees that

$$\lim_{\varepsilon \to 0} \frac{1}{\varepsilon}(V_d(\mathbb{K} + \varepsilon\mathbb{B}^d) - V_d(\mathbb{K})) = \kappa_1 V_{d-1}(\mathbb{K}), \tag{7}$$

and from (4) that $\kappa_1 = 2$. Hence $V_{d-1}(\mathbb{K})$ may be viewed as half the surface area. The functional $V_1(\mathbb{K})$ is related to the mean width $w(\mathbb{K})$ defined as the mean value of the distance between a pair of parallel support planes of $\mathbb{K}$. The relation is

$$V_1(\mathbb{K}) = \frac{d\kappa_d}{2\kappa_{d-1}} w(\mathbb{K}), \tag{8}$$

which reduces to $V_1(\mathbb{K}) = w(\mathbb{K})/2$ for $d = 3$. Finally the functional $V_0(\mathbb{K})$ is evaluated from (5) by dividing with ε^d and taking the limit $\varepsilon \to \infty$. It follows that $V_0(\mathbb{K}) = 1$ for all $\mathbb{K} \in \mathcal{K} \setminus \{\emptyset\}$. One extends V_0 to all of $\mathcal{K}$ by defining $V_0(\emptyset) = 0$. The geometric observable V_0 is called Euler characteristic.

The geometric observables V_i have several important properties. They are Euclidean invariant (i.e. invariant under rigid motions), additive and monotone. Let $T_d \cong (\mathbb{R}^d, +)$ denote the group of translations with vector addition as group operation and let $\mathrm{SO}(d)$ be the matrix group of rotations in d dimensions (Barut and Raczka, 1986). The semidirect product $E_d = T_d \odot \mathrm{SO}(d)$ is the Euclidean group of rigid motions in $\mathbb{R}^d$. It is defined as the set of pairs $(\boldsymbol{a}, A)$ with $\boldsymbol{a} \in \mathrm{T}_d$ and $A \in \mathrm{SO}(d)$ and group operation

$$(\boldsymbol{a}, A) \circ (\boldsymbol{b}, B) = (\boldsymbol{a} + A\boldsymbol{b}, AB). \tag{9}$$

An observable $f\colon \mathcal{K} \to \mathbb{R}$ is called Euclidean invariant or invariant under rigid motions if

$$f(\boldsymbol{a} + A\mathbb{K}) = f(\mathbb{K}), \tag{10}$$

holds for all $(\boldsymbol{a}, A) \in E_d$ and all $\mathbb{K} \in \mathcal{K}$. Here $A\mathbb{K} = \{A\boldsymbol{x}: \boldsymbol{x} \in \mathbb{K}\}$ denotes the rotation of $\mathbb{K}$ and $\boldsymbol{a} + \mathbb{K} = \{\boldsymbol{a}\} + \mathbb{K}$ its translation. A geometric observable f is called additive if

$$f(\emptyset) = 0, \tag{11}$$

$$f(\mathbb{K}_1 \cup \mathbb{K}_2) + f(\mathbb{K}_1 \cap \mathbb{K}_2) = f(\mathbb{K}_1) + f(\mathbb{K}_2), \tag{12}$$

holds for all $\mathbb{K}_1, \mathbb{K}_2 \in \mathcal{K}$ with $\mathbb{K}_1 \cup \mathbb{K}_2 \in \mathcal{K}$. Finally a functional is called monotone if for $\mathbb{K}_1, \mathbb{K}_2 \in \mathcal{K}$ with $\mathbb{K}_1 \subset \mathbb{K}_2$ follows $f(\mathbb{K}_1) \leqslant f(\mathbb{K}_2)$.

The special importance of the functionals $V_i(\mathbb{K})$ arises from the following theorem of Hadwiger (Hadwiger, 1955). A functional $f: \mathcal{K} \to \mathbb{R}$ is Euclidean invariant, additive and monotone if it is a linear combination

$$f = \sum_{i=0}^{d} c_i V_i, \tag{13}$$

with non-negative constants $c_0, \ldots, c_d$. The condition of monotonicity can be replaced with continuity at the expense of allowing also negative c_i, and the theorem remains valid (Hadwiger, 1995). If f is continuous on $\mathcal{K}$, additive and Euclidean invariant it can be additively extended to the convex ring $\mathcal{R}$ (Schneider and Weil, 1992). The additive extension is unique and given by the inclusion-exclusion formula

$$f\left(\bigcup_{i=1}^{m} \mathbb{K}_1\right) = \sum_{\mathbb{I} \in \mathcal{P}(m)} (-1)^{|\mathbb{I}|-1} f\left(\bigcap_{i \in \mathbb{I}} \mathbb{K}_i\right), \tag{14}$$

where $\mathcal{P}(m)$ denotes the family of nonempty subsets of $\{1, \ldots, m\}$ and $|\mathbb{I}|$ is the number of elements of $\mathbb{I} \in \mathcal{P}(m)$. In particular, the functionals V_i have a unique additive extension to the convex ring $\mathcal{R}$(Schneider and Weil, 1992), which is again denoted by V_i.

For a three-dimensional porous sample with $\mathbb{P} \in \mathcal{R}$ the extended functionals V_i lead to two frequently used geometric observables. The first is the porosity of a porous sample $\mathbb{S}$ defined as

$$\phi(\mathbb{P} \cap \mathbb{S}) = \phi_3(\mathbb{P} \cap \mathbb{S}) = \frac{V_3(\mathbb{P} \cap \mathbb{S})}{V_3(\mathbb{S})}, \tag{15}$$

and the second its specific internal surface area which may be defined in view of (7) as

$$\phi_2(\mathbb{P} \cap \mathbb{S}) = \frac{2V_2(\mathbb{P} \cap \mathbb{S})}{V_3(\mathbb{S})}. \tag{16}$$

The two remaining observables $\phi_1(\mathbb{P} \cap \mathbb{S}) = V_1(\mathbb{P} \cap \mathbb{S})/V_3(\mathbb{S})$ and $\phi_0(\mathbb{P} \cap \mathbb{S}) = V_0(\mathbb{P} \cap \mathbb{S})/V_3(\mathbb{S})$ have received less attention in the porous media literature. The

Euler characteristic V_0 on $\mathcal{R}$ coincides with the identically named topological invariant. For $d = 2$ and $\mathbb{G} \in \mathcal{R}$ one has $V_0(\mathbb{G}) = c(\mathbb{G}) - c'(\mathbb{G})$ where $c(\mathbb{G})$ is the number of connectedness components of $\mathbb{G}$, and $c'(\mathbb{G})$ denotes the number of holes (i.e. bounded connectedness components of the complement).

3.3. DEFINITION OF STOCHASTIC POROUS MEDIA

For theoretical purposes the pore space $\mathbb{P}$ is frequently viewed as a random set (Stoyan *et al.*, 1995; Hilfer, 1996). In practical applications the pore space is usually discretized because of measurement limitations and finite resolution. For the purpose of discussion the set $\mathbb{S} \subset \mathbb{R}^3$ is a rectangular parallelepiped whose side-lengths are M_1, M_2 and M_3 in units of the lattice constant a (resolution) of a simple cubic lattice. The position vectors $\boldsymbol{r}_i = \boldsymbol{r}_{i_1 \ldots i_d} = (ai_1, \ldots, ai_d)$ with integers $1 \leqslant i_j \leqslant M_j$ are used to label the lattice points, and $\boldsymbol{r}_i$ is a shorthand notation for $\boldsymbol{r}_{i_1 \ldots i_d}$. Let $\mathbb{V}_i$ denote a cubic volume element (voxel) centered at the lattice site $\boldsymbol{r}_i$. Then the discretized sample may be represented as $\mathbb{S} = \bigcup_{i=1}^{N} \mathbb{V}_i$. The discretized pore space $\widetilde{\mathbb{P}}$, defined as

$$\widetilde{\mathbb{P}} = \bigcup_{\{i:\ \chi_{\mathbb{P}}(\boldsymbol{r}_i)=1\}} \mathbb{V}_i, \tag{17}$$

is an approximation to the true pore space $\mathbb{P}$. For simplicity it will be assumed that the discretization does not introduce errors, that is that $\widetilde{\mathbb{P}} = \mathbb{P}$, and that each voxel is either fully pore or fully matrix. This assumption may be relaxed to allow voxel attributes such as internal surface or other quermassintegral densities. The discretization into voxels reflects the limitations arising from the experimental resolution of the porous structure. A discretized pore space for a bounded sample belongs to the convex ring $\mathcal{R}$ if the voxels are convex and compact. Hence, for a simple cubic discretization the pore space belongs to the convex ring. A configuration (or microstructure) $\boldsymbol{Z}$ of a 2-component medium may be represented in the simplest case by a sequence

$$\boldsymbol{Z} = (Z_1, \ldots, Z_N) = (\chi_{\mathbb{P}}(\boldsymbol{r}_1), \ldots, \chi_{\mathbb{P}}(\boldsymbol{r}_N)), \tag{18}$$

where $\boldsymbol{r}_i$ runs through the lattice points and $N = M_1 M_2 M_3$. This representation corresponds to the simplest discretization in which there are only two states for each voxel indicating whether it belongs to pore space or not. In general a voxel could be characterized by more states reflecting the microsctructure within the region $\mathbb{V}_i$. In the simplest case there is a one-to-one correspondence between $\mathbb{P}$ and $\boldsymbol{Z}$ given by (18). Geometric observables $f(\mathbb{P})$ then correspond to functions $f(\boldsymbol{Z}) = f(z_1, \ldots, z_N)$.

As a convenient theoretical idealization it is frequently assumed that porous media are random realizations drawn from an underlying statistical ensemble. A

discretized stochastic porous medium is defined through the discrete probability density

$$p(z_1, \ldots, z_N) = \text{Prob}\{(Z_1 = z_1) \wedge \ldots \wedge (Z_N = z_N)\}, \tag{19}$$

where $z_i \in \{0, 1\}$ in the simplest case. It should be emphasized that the probability density p is mainly of theoretical interest. In practice p is usually not known. An infinitely extended medium or microstructure is called stationary or statistically homogeneous if p is invariant under spatial translations. It is called isotropic if p is invariant under rotations.

3.4. MOMENT FUNCTIONS AND CORRELATION FUNCTIONS

A stochastic medium was defined through its probability distribution p. In practice p will be even less accessible than the microstructure $\mathbb{P} = \boldsymbol{Z}$ itself. Partial information about p can be obtained by measuring or calculating expectation values of a geometric observable f. These are defined as

$$\langle f(z_1, \ldots, z_N)\rangle = \sum_{z_1=0}^{1} \cdots \sum_{z_N=0}^{1} f(z_1, \ldots, z_N) p(z_1, \ldots, z_N), \tag{20}$$

where the summations indicate a summation over all configurations. Consider, for example, the porosity $\phi(\mathbb{S})$ defined in (15). For a stochastic medium $\phi(\mathbb{S})$ becomes a random variable. Its expectation is

$$\begin{aligned}
\langle\phi\rangle &= \frac{\langle V_3(\mathbb{P})\rangle}{V_3(\mathbb{S})} = \frac{1}{V_3(\mathbb{S})} \int_{\mathbb{S}} \langle \chi_{\mathbb{P}}(\boldsymbol{r})\rangle \, \mathrm{d}^3\boldsymbol{r} \\
&= \frac{1}{V_3(\mathbb{S})} \sum_{i=1}^{N} \langle z_i\rangle V_3(\mathbb{V}_i) = \frac{1}{N} \sum_{i=1}^{N} \langle z_i\rangle \\
&= \frac{1}{N} \sum_{i=1}^{N} \text{Prob}\{z_i = 1\} = \frac{1}{N} \sum_{i=1}^{N} \text{Prob}\{\boldsymbol{r}_i \in \mathbb{P}\}.
\end{aligned} \tag{21}$$

If the medium is statistically homogeneous then

$$\langle\phi\rangle = \text{Prob}\{z_i = 1\} = \text{Prob}\{\boldsymbol{r}_i \in \mathbb{P}\} = \langle \chi_{\mathbb{P}}(\boldsymbol{r}_i)\rangle, \tag{22}$$

independent of i. It happens frequently that one is given only a single sample, not an ensemble of samples. It is then necessary to invoke an ergodic hypothesis that allows to equate spatial averages with ensemble averages.

The porosity is the first member in a hierarchy of moment functions. The nth order moment function is defined generally as

$$S_n(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n) = \langle \chi_{\mathbb{P}}(\boldsymbol{r}_1) \ldots \chi_{\mathbb{P}}(\boldsymbol{r}_n)\rangle, \tag{23}$$

for $n \leqslant N$.[2] For stationary media $S_n(\boldsymbol{r}_1, \ldots \boldsymbol{r}_n) = g(\boldsymbol{r}_1 - \boldsymbol{r}_n, \ldots, \boldsymbol{r}_{n-1} - \boldsymbol{r}_n)$ where the function g depends only on $n-1$ variables. Another frequently used expectation value is the correlation function which is related to S_2. For a homogeneous medium it is defined as

$$\begin{aligned} G(\boldsymbol{r}_0, \boldsymbol{r}) &= G(\boldsymbol{r} - \boldsymbol{r}_0) = \frac{\langle \chi_{\mathbb{P}}(\boldsymbol{r}_0)\chi_{\mathbb{P}}(\boldsymbol{r})\rangle - \langle\phi\rangle^2}{\langle\phi\rangle(1 - \langle\phi\rangle)} \\ &= \frac{S_2(\boldsymbol{r} - \boldsymbol{r}_0) - (S_1(\boldsymbol{r}_0))^2}{S_1(\boldsymbol{r}_0)(1 - S_1(\boldsymbol{r}_0))}, \end{aligned} \tag{24}$$

where $\boldsymbol{r}_0$ is an arbitrary reference point, and $\langle\phi\rangle = S_1(\boldsymbol{r}_0)$. If the medium is isotropic then $G(\boldsymbol{r}) = G(|\boldsymbol{r}|) = G(r)$. Note that G is normalized such that $G(0) = 1$ and $G(\infty) = 0$.

The hierarchy of moment functions S_n, similar to p, is mainly of theoretical interest. For a homogeneous medium S_n is a function of $n-1$ variables. To specify S_n numerically becomes impractical as n increases. If only 100 points are required along each coordinate axis then giving S_n would require $10^{2d(n-1)}$ numbers. For $d = 3$ this implies that already at $n = 3$ it becomes economical to specify the microstructure $\mathbb{P}$ directly rather than incompletely through moment or correlation functions.

3.5. CONTACT DISTRIBUTIONS

An interesting geometric characteristic introduced and discussed in the field of stochastic geometry are contact distributions (Delfiner, 1972; Stoyan *et al.*, 1995; p. 206). Certain special cases of contact distributions have appeared also in the porous media literature (Dullien, 1992). Let $\mathbb{G}$ be a compact test set containing the origin $\mathbf{0}$. Then the contact distribution is defined as the conditional probability

$$\begin{aligned} H_{\mathbb{G}}(r) &= 1 - \text{Prob}\{\mathbf{0} \notin \mathbb{M} + (-r\mathbb{G}) | \mathbf{0} \notin \mathbb{M}\} \\ &= 1 - \frac{\text{Prob}\{\mathbb{M} \cap r\mathbb{G} = \emptyset\}}{\phi}. \end{aligned} \tag{25}$$

If one defines the random variable $R = \inf\{s\colon \mathbb{M} \cap s\mathbb{G} \neq \emptyset\}$ then $H_{\mathbb{G}}(r) = \text{Prob}\{R \leqslant r | R > 0\}$ (Stoyan *et al.*, 1995).

For the unit ball $\mathbb{G} = \mathbb{B}(\mathbf{0}, 1)$ in three dimensions $H_{\mathbb{B}}$ is called spherical contact distribution. The quantity $1 - H_{\mathbb{B}}(r)$ is then the distribution function of the random distance from a randomly chosen point in $\mathbb{P}$ to its nearest neighbour in $\mathbb{M}$. The probability density

$$p(r) = \frac{\mathrm{d}}{\mathrm{d}r}(1 - H_{\mathbb{B}}(r)) = -\frac{\mathrm{d}}{\mathrm{d}r}H_{\mathbb{B}}(r), \tag{26}$$

[2] If a voxel has other attributes besides being pore or matrix one may define also mixed moment functions $S_{i_1 \ldots i_n}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n) = \langle \phi_{i_1}(\boldsymbol{r}_1) \ldots \phi_{i_n}(\boldsymbol{r}_n)\rangle$ where $\phi_i(\boldsymbol{r}_j) = V_i(\mathbb{P} \cap \mathbb{V}_j)/V_i(\mathbb{V}_j)$ for $i = 1, \ldots d$ are the quermassintegral densities for the voxel at site $\boldsymbol{r}_j$.

was discussed in (Scheidegger, 1974) as a well defined alternative to the frequently used pore-size distribution from mercury porosimetry.

For an oriented unit interval $\mathbb{G} = \mathbb{B}^1(\mathbf{0}, 1; \boldsymbol{e})$ where $\boldsymbol{e}$ is the unit vector one obtains the linear contact distribution. The linear contact distribution written as $L(r\boldsymbol{e}) = \phi(1 - H_{\mathbb{B}^1(\mathbf{0},1;\boldsymbol{e})}(r))$ is sometimes called lineal path function (Yeong and Torquato, 1998). It is related to the chord length distribution $p_{cl}(x)$ defined as the probability that an interval in the intersection of $\mathbb{P}$ with a straight line containing $\mathbb{B}^1(\mathbf{0}, 1, \boldsymbol{e})$ has length smaller than x (Stoyan *et al.*, 1995; Hilfer, 1996, p. 208).

3.6. LOCAL POROSITY DISTRIBUTIONS

The idea of local porosity distributions is to measure geometric observables inside compact convex subsets $\mathbb{K} \subset \mathbb{S}$, and to collect the results into empirical histograms (Hilfer, 1991). Let $\mathbb{K}(\boldsymbol{r}, L)$ denote a cube of side length L centered at the lattice vector $\boldsymbol{r}$. The set $\mathbb{K}(\boldsymbol{r}, L)$ is called a measurement cell. A geometric observable f, when measured inside a measurement cell $\mathbb{K}(\boldsymbol{r}, L)$, is denoted as $f(\boldsymbol{r}, L)$ and called a local observable. An example are local Hadwiger functional densities $f = \sum_{i=0}^{d} c_i \psi_i$ with coefficients c_i as in Hadwigers theorem (13). Here the local quermassintegrals are defined using (6) as

$$\psi_i(\mathbb{P} \cap \mathbb{K}(\boldsymbol{r}, L)) = \frac{W_i(\mathbb{P} \cap \mathbb{K}(\boldsymbol{r}, L))}{V_d(\mathbb{K}(\boldsymbol{r}, L))}, \tag{27}$$

for $i = 0, \ldots, d$. In the following mainly the special case $d = 3$ will be of interest. For $d = 3$ the local porosity is defined by setting $i = 0$,

$$\phi(\boldsymbol{r}, L) = \psi_0(\mathbb{P} \cap \mathbb{K}(\boldsymbol{r}, L)). \tag{28}$$

Local densities of surface area, mean curvature and Euler characteristic may be defined analogously. The local porosity distribution, defined as

$$\mu(\phi; \boldsymbol{r}, L) = \langle \delta(\phi - \phi(\boldsymbol{r}, L)) \rangle, \tag{29}$$

gives the probability density to find a local porosity $\phi(\boldsymbol{r}, L)$ in the measurement cell $\mathbb{K}(\boldsymbol{r}, L)$. Here $\delta(x)$ denotes the Dirac δ-distribution. The support of μ is the unit interval. For noncubic measurement cells $\mathbb{K}$ one defines analogously $\mu(\phi; \mathbb{K}) = \langle \delta(\phi - \phi(\mathbb{K})) \rangle$ where $\phi(\mathbb{K}) = \phi(\mathbb{P} \cap \mathbb{K})$ is the local observable in cell $\mathbb{K}$.

The concept of local porosity distributions[3] was introduced in (Hilfer, 1991) and has been generalized in two directions (Hilfer, 1996). Firstly by admitting more than one measurement cell, and secondly by admitting more than one geometric observable. The general n-cell distribution function is defined as (Hilfer, 1996)

$$\begin{aligned} &\mu_{n;f_1,\ldots,f_m}(f_{11}, \ldots, f_{1n}; \ldots; f_{n1}, \ldots, f_{nm}; \mathbb{K}_1, \ldots, \mathbb{K}_n) \\ &\quad = \langle \delta(f_{11} - f_1(\mathbb{K}_1)) \ldots \delta(f_{1n} - f_1(\mathbb{K}_n)) \ldots \delta(f_{m1} - f_1(\mathbb{K}_1)) \ldots \\ &\qquad \delta(f_{mn} - f_m(\mathbb{K}_n)) \rangle, \end{aligned} \tag{30}$$

[3] or more generally 'local geometry distributions' (Hilfer, 1992; Hilfer, 1996).

for n general measurement cells $\mathbb{K}_1, \ldots, \mathbb{K}_n$ and m observables $f_1, \ldots, f_m$. The n-cell distribution is the probability density to find the values f_{11} of the local observable f_1 in cell $\mathbb{K}_1$ and f_{12} in cell $\mathbb{K}_2$ and so on until f_{mn} of local observable f_m in $\mathbb{K}_n$. Definition (30) is a broad generalization of (29). This generalization is not purely academic, but was motivated by problems of fluid flow in porous media where not only ψ_0 but also ψ_1 becomes important (Hilfer, 1992). Local quermassintegrals, defined in (27), and their linear combinations (Hadwiger functionals) furnish important examples for local observables in (30), and they have recently been measured on real sandstone samples (Manwart and Hilfer, 1999).

The general n-cell distribution in (30) is very general indeed. It even contains p from (19) as the special case $m = 1$, $f_1 = \phi$ and $n = N$ with $\mathbb{K}_i = \mathbb{V}_i = \mathbb{K}(\boldsymbol{r}_i, a)$. More precisely one has

$$\mu_{N;\phi}(\phi_1, \ldots, \phi_N; \mathbb{V}_1, \ldots, \mathbb{V}_N) = p(\phi_1, \ldots, \phi_N), \tag{31}$$

because in that case $\phi_i = z_i = 1$, if $\mathbb{V}_i \in \mathbb{P}$ and $\phi_i = z_i = 0$ for $\mathbb{V} \notin \mathbb{P}$. In this way one sees that the very definition of a stochastic geometry is related to local-porosity distributions (or more generally local-geometry distributions). As a consequence the general n-cell distribution $\mu_{n;f_1,\ldots,f_m}$ is again mainly of theoretical interest, and usually unavailable for practical computations.

Expectation values with respect to p have generalizations to averages with respect to μ. Averaging with respect to μ will be denoted by an overline. In the special case $m = 1$, $f_1 = \phi$ and $\mathbb{K}_i = \mathbb{V}_i = \mathbb{K}(\boldsymbol{r}_i, a)$ with $n < N$ one finds (Hilfer, 1996)

$$\begin{aligned}
&\overline{\phi(\boldsymbol{r}_1, a) \cdots \phi(\boldsymbol{r}_n, a)} \\
&= \int_0^1 \cdots \int_0^1 \phi_1 \cdots \phi_n \mu_{n;\phi}(\phi_1, \ldots, \phi_n; \mathbb{V}_1, \ldots, \mathbb{V}_n) \mathrm{d}\phi_1 \cdots \mathrm{d}\phi_n \\
&= \int_0^1 \cdots \int_0^1 \phi_1 \cdots \phi_n \mu_{N;\phi}(\phi_1, \ldots, \phi_N; \mathbb{V}_1, \ldots, \mathbb{V}_N) \mathrm{d}\phi_1 \cdots \mathrm{d}\phi_N \\
&= \int_0^1 \cdots \int_0^1 \phi_1 \cdots \phi_n \langle \delta(\phi_1 - \phi(\boldsymbol{r}_1, a)) \cdots \delta(\phi_N - \phi(\boldsymbol{r}_N, a)) \rangle \mathrm{d}\phi_1 \cdots \mathrm{d}\phi_N \\
&= \langle \phi(\boldsymbol{r}_1, a) \cdots \phi(\boldsymbol{r}_n, a) \rangle \\
&= \langle \chi_{\mathbb{P}}(\boldsymbol{r}_1) \ldots \chi_{\mathbb{P}}(\boldsymbol{r}_n) \rangle \\
&= S_n(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n),
\end{aligned} \tag{32}$$

thereby identifying the moment functions of order n as averages with respect to an n-cell distribution.

For practical applications the 1-cell local-porosity distributions $\mu(\boldsymbol{r}, L)$ and their analogues for other quermassintegrals are of greatest interest. For a homogeneous medium the local-porosity distribution obeys

$$\mu(\phi; \boldsymbol{r}, L) = \mu(\phi; \boldsymbol{0}, L) = \mu(\phi; L), \tag{33}$$

for all lattice vectors $\boldsymbol{r}$. Thus it is independent of the placement of the measurement cell. A disordered medium with substitutional disorder (Ziman, 1982) may be viewed as a stochastic geometry obtained by placing random elements at the cells or sites of a fixed regular substitution lattice. For a substitutionally disordered medium the local-porosity distribution $\mu(\phi_i; \boldsymbol{r}, L)$ is a periodic function of $\boldsymbol{r}$ whose period is the lattice constant of the substitution lattice. For stereological issues in the measurement of μ from thin sections see (Virgin *et al.*, 1996).

Averages with respect to μ are denoted by an overline. For a homogeneous medium the average local porosity is found as

$$\overline{\phi}(\boldsymbol{r}, L) = \int_0^1 \mu(\phi; \boldsymbol{r}, L)\mathrm{d}\phi = \langle\phi\rangle = \overline{\phi}, \tag{34}$$

independent of $\boldsymbol{r}$ and L. The variance of local porosities for a homogeneous medium defined in the first equality

$$\begin{aligned}\sigma^2(L) &= \overline{(\phi(L) - \overline{\phi})^2} \\ &= \int_0^1 (\phi(L) - \overline{\phi})^2 \mu(\phi; L)\,\mathrm{d}\phi \\ &= \frac{1}{L^3}\langle\phi\rangle(1 - \langle\phi\rangle)\left(1 + \frac{2}{L^3}\sum_{\substack{r_i, r_j \in \mathbb{K}(r_0, L) \\ i \neq j}} G(\boldsymbol{r}_i - \boldsymbol{r}_j)\right),\end{aligned} \tag{35}$$

is related to the correlation function as given in the second equality (Hilfer, 1996). The skewness of the local-porosity distribution is defined as the average

$$\kappa_3(L) = \frac{\overline{(\phi(L) - \overline{\phi})^3}}{\sigma(L)^3}. \tag{36}$$

The limits $L \to 0$ and $L \to \infty$ of small and large measurement cells are of special interest. In the first case one reaches the limiting resolution at $L = a$ and finds for a homogeneous medium (Hilfer, 1991, 1996)

$$\mu(\phi; a) = \overline{\phi}\delta(\phi - 1) - (1 - \overline{\phi})\delta(\phi). \tag{37}$$

The limit $L \to \infty$ is more intricate because it requires also the limit $\mathbb{S} \to \mathbb{R}^3$. For a homogeneous medium (35) shows $\sigma(L) \to 0$ for $L \to \infty$ and this suggests

$$\mu(\phi; L \to \infty) = \delta(\phi - \overline{\phi}). \tag{38}$$

For macroscopically heterogeneous media, however, the limiting distribution may deviate from this result (Hilfer, 1996). If (38) holds then in both limits the geometrical information contained in μ reduces to the single number $\overline{\phi} = \langle\phi\rangle$. If (37) and (38) hold there exists a special length scale L^* defined as

$$L^* = \min\{L\colon\ \mu(0; L) = \mu(1; L) = 0\}, \tag{39}$$

at which the δ-components at $\phi = 0$ and $\phi = 1$ vanish. The length L^* is a measure for the size of pores.

The ensemble picture underlying the definition of a stochastic medium is an idealization. In practice one is given only a single realization and has to resort to an ergodic hypothesis for obtaining an estimate of the local-porosity distributions. The local-porosity distribution may then be estimated by

$$\widetilde{\mu}(\phi; L) = \frac{1}{m} \sum_{r} \delta(\phi - \phi(\boldsymbol{r}, L)), \tag{40}$$

where m is the number of placements of the measurement cell $\mathbb{K}(\boldsymbol{r}, L)$. Ideally the measurement cells should be far apart or at least nonoverlapping, but in practice this restriction cannot be observed because the samples are not large enough. The use of $\widetilde{\mu}$ instead of μ can lead to deviations due to violations of the ergodic hypothesis or simply due to oversampling the central regions of $\mathbb{S}$ (Biswal *et al.*, 1998, 1999).

3.7. LOCAL PERCOLATION PROBABILITIES

Transport and propagation in porous media are controlled by the connectivity of the pore space. Local percolation probabilities characterize the connectivity (Hilfer, 1991). Their calculation requires a three-dimensional pore space representation, and early results were restricted to samples reconstructed laboriously from sequential thin sectioning (Hilfer *et al.*, 1997) In this section a relationship between the Euler characteristic and the local percolation probabililties is established for the first time.

Consider the functional $\Lambda\colon \mathcal{K} \times \mathcal{K} \times \mathcal{R} \to \mathbb{Z}_2 = \{0, 1\}$ defined by

$$\Lambda(\mathbb{K}_0, \mathbb{K}_\infty; \mathbb{P} \cap \mathbb{S}) = \begin{cases} 1\colon & \text{if } \mathbb{K}_0 \rightsquigarrow \mathbb{K}_\infty \text{ in } \mathbb{P} \\ 0\colon & \text{otherwise} \end{cases} \tag{41}$$

where $\mathbb{K}_0 \subset \mathbb{R}^3, \mathbb{K}_\infty \subset \mathbb{R}^3$ are two compact convex sets with $\mathbb{K}_0 \cap (\mathbb{P} \cap \mathbb{S}) \neq \emptyset$ and $\mathbb{K}_\infty \cap (\mathbb{P} \cap \mathbb{S}) \neq \emptyset$, and '$\mathbb{K}_0 \rightsquigarrow \mathbb{K}_\infty$ in $\mathbb{P}$' means that there is a path connecting $\mathbb{K}_0$ and $\mathbb{K}_\infty$ that lies completely in $\mathbb{P}$. In the examples below the sets $\mathbb{K}_0$ and $\mathbb{K}_\infty$ correspond to opposite faces of the sample, but in general other choices are allowed. Analogous to Λ, which is defined for the whole sample, one defines for a measurement cell

$$\Lambda_\alpha(\boldsymbol{r}, L) = \Lambda(\mathbb{K}_{0\alpha}, \mathbb{K}_{\infty\alpha}; \mathbb{P} \cap \mathbb{K}(\boldsymbol{r}, L)) = \begin{cases} 1\colon & \text{if } \mathbb{K}_{0\alpha} \rightsquigarrow \mathbb{K}_{\infty\alpha} \text{ in } \mathbb{P} \\ 0\colon & \text{otherwise} \end{cases} \tag{42}$$

where $\alpha = x, y, z$ and $\mathbb{K}_{0x}, \mathbb{K}_{\infty x}$ denote those two faces of $\mathbb{K}(\boldsymbol{r}, L)$ that are normal to the x-direction. Similarly $\mathbb{K}_{0y}, \mathbb{K}_{\infty y}, \mathbb{K}_{0z}\mathbb{K}_{\infty z}$ denote the faces of $\mathbb{K}(\boldsymbol{r}, L)$ normal to the y- and z-directions. Two additional percolation observables Λ_3 and Λ_c are introduced by

$$\Lambda_3(\boldsymbol{r}, L) = \Lambda_x(\boldsymbol{r}, L)\Lambda_y(\boldsymbol{r}, L)\Lambda_z(\boldsymbol{r}, L), \tag{43}$$

$$\Lambda_c(\boldsymbol{r}, L) = \operatorname{sgn}(\Lambda_x(\boldsymbol{r}, L) + \Lambda_y(\boldsymbol{r}, L) + \Lambda_z(\boldsymbol{r}, L)). \tag{44}$$

Λ_3 indicates that the cell is percolating in all three directions while Λ_c indicates percolation in x-, or y- or z-direction. The local percolation probabilities are defined as

$$\lambda_\alpha(\phi; L) = \frac{\sum_{\boldsymbol{r}} \Lambda_\alpha(\boldsymbol{r}, L)\delta_{\phi,\phi(\boldsymbol{r},L)}}{\sum_{\boldsymbol{r}} \delta_{\phi,\phi(\boldsymbol{r},L)}}, \tag{45}$$

where

$$\delta_{\phi,\phi(\boldsymbol{r},L)} = \begin{cases} 1: & \text{if } \phi = \phi(\boldsymbol{r}, L) \\ 0: & \text{otherwise.} \end{cases} \tag{46}$$

The local percolation probability $\lambda_\alpha(\phi; L)$ gives the fraction of measurement cells of sidelength L with local porosity ϕ that are percolating in the 'α'-direction. The total fraction of cells percolating along the 'α'-direction is then obtained by integration

$$p_\alpha(L) = \int_0^1 \mu(\phi; L)\lambda_\alpha(\phi; L)\mathrm{d}\phi. \tag{47}$$

This geometric observable is a quantitative measure for the number of elements that have to be percolating if the pore space geometry is approximated by a substitutionally disordered lattice or network model. Note that neither Λ nor Λ_α are additive functionals, and hence local-percolation probabilities are not covered by Hadwigers theorem.

It is interesting that there is a relation between the local-percolation probabilities and the local Euler characteristic $V_0(\mathbb{P} \cap \mathbb{K}(\boldsymbol{r}, l))$. The relation arises from the observation that the voxels $\mathbb{V}_i$ are closed, convex sets, and hence for any two voxels $\mathbb{V}_i, \mathbb{V}_j$ the Euler characteristic of their intersection

$$V_0(\mathbb{V}_i \cap \mathbb{V}_j) = \begin{cases} 1: & \text{if } \mathbb{V}_i \cap \mathbb{V}_j \neq \emptyset \\ 0: & \text{if } \mathbb{V}_i \cap \mathbb{V}_j = \emptyset \end{cases} \tag{48}$$

indicates whether two voxels are nearest neighbours. A measurement cell $\mathbb{K}(\boldsymbol{r}, L)$ contains L^3 voxels. It is then possible to construct a $(L^3 + 2) \times (L^3 + 2)^2$-matrix B with matrix elements

$$(B)_{i\,(i,j)} = V_0(\mathbb{V}_i \cap \mathbb{V}_j) \tag{49}$$

$$(B)_{i\,(j,i)} = -V_0(\mathbb{V}_i \cap \mathbb{V}_j) \tag{50}$$

where $i, j \in \{0, 1, \ldots, L^3, \infty\}$ and the sets $\mathbb{V}_0 = \mathbb{K}_0$ and $\mathbb{V}_\infty = \mathbb{K}_\infty$ are two opposite faces of the measurement cell. The rows in the matrix B correspond to voxels while the columns correspond to voxel pairs. Define the matrix $A = BB^T$

where B^T is the transpose of B. The diagonal elements $(A)_{ii}$ give the number of voxels to which the voxel $\mathbb{V}_i$ is connected. A matrix element $(A)_{ij}$ differs from zero if and only if $\mathbb{V}_i$ and $\mathbb{V}_j$ are connected. Hence the matrix A reflects the local connectedness of the pore space around a single voxel. Sufficiently high powers of A provide information about the global connectedness of $\mathbb{P}$. One finds

$$\Lambda(\mathbb{K}_0, \mathbb{K}_\infty; \mathbb{P} \cap \mathbb{K}(\boldsymbol{r}, L)) = \operatorname{sgn}(|(A^m)_{0\infty}|), \tag{51}$$

where $(A^m)_{0\infty}$ is the matrix element in the upper right-hand corner and m is arbitrary subject to the condition $m > \mathrm{L}^3$. The set $\mathbb{P} \cap \mathbb{K}(\boldsymbol{r}, L)$ can always be decomposed uniquely into pairwise disjoint connectedness components (clusters) $\mathbb{B}_i$ whose number is given by the rank of B. Hence

$$V_0(\mathbb{P} \cap \mathbb{K}(\boldsymbol{r}, L)) = \sum_{i=1}^{\operatorname{rank} B} V_0(\mathbb{B}_i), \tag{52}$$

provides an indirect connection between the local Euler characteristic and the local-percolation probabilities mediated by the matrix B.[4]

The theoretical concepts for the geometric characterization of porous media discussed here are also useful in effective medium calculations of transport parameters such as conductivity or permeability (Hilfer, 1991, 1992, 1996). The resulting parameterfree predictions agree well with the exact result (Widjajakusuma *et al.*, 1999a, b).

4. Application Example

The purpose of this section is to show that the previous theoretical framework can be used directly for predicting transport in porous media quantitatively and without free macroscopic fit parameters. The theory presented above allows a quantitative micro-macro transition in porous media and opens the possibility to determine the elusive 'representative elementary volume' needed for macroscopic theories in a quantitative and property specific manner.

In (Biswal *et al.*, 1999) a fully three-dimensional experimental sample of Fontainebleau sandstone was compared with three geometric models, some of which had not only the same porosity and specific internal surface area but also the same correlation function $G(r)$. A large number of the geometric quantities discussed above was calculated in (Biswal *et al.*, 1999). For a discussion on the influence of contact distributions see (Manwart *et al.*, 2000). The total fraction of percolating cells, defined in Equation (47) above, was measured in (Biswal *et al.*, 1999) for Fontainebleau and some of its models. Figure 1 shows the total fraction of percolating cells as a function of length scale (side length of measurement cells).

[4]For percolation systems it has been conjectured that the zero of the Euler characteristic as a function of the occupation probability is an approximation to the percolation threshold (Mecke and Wagner, 1991).

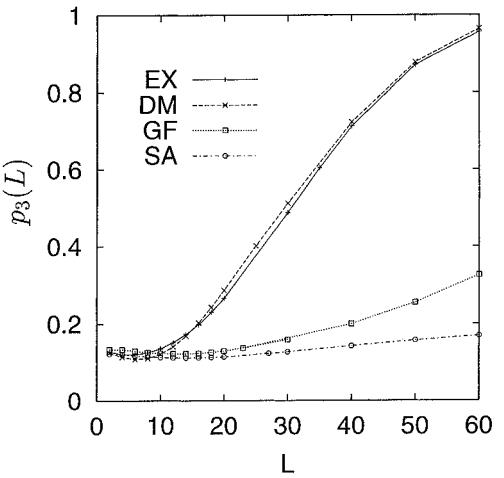

Figure 1. Total fraction of percolating cells for Fontainebleau sandstone (EX) and three of its models (DM, GF, SA) as discussed in Ref. (Biswal *et al.*, 1999).

It turns out that the quantity $p_3(L)$ displayed in Figure 1 correlates very well with transport properties such as the hydraulic permeability. Recently transport properties such as the permeabilities and formation factors of the Fontainebleau sandstone and its geometries were calculated numerically exactly by solving the appropriate microscopic equations of motion on the computer (Manwart and Hilfer, 1999). Some of the results are summarized in Table I below.

One sees from Table I that while EX and DM are very similar in their permeabilities and formation factors the samples EX and GF have significantly lower values with GF being somewhat higher than SA. The same relationship is observed in Figure 1 for the percolation properties. These results show that the purely

Table I. Physical transport properties of Fontainebleau sandstone and three geometric models for it (see (Biswal *et al.*, 1999)). σ_{ii} is the conductivity in the direction $i = x, y, z$ in units of $10^{-3}\sigma_{\mathbb{P}}$, where $\sigma_{\mathbb{P}}$ is the conductivity of the material filling the pore space. k_{ii} is the permeability in the direction $i = x, y, z$ in mD.

	EX	DM	SA	GF
k_{zz}[mD]	692	923	35	34
k_{yy}[mD]	911	581	22	35
k_{xx}[mD]	790	623	20	36
$\sigma_{zz}[10^{-3}\sigma_{\mathbb{P}}]$	18.5	26.2	1.35	2.05
$\sigma_{yy}[10^{-3}\sigma_{\mathbb{P}}]$	21.9	17.0	0.87	1.97
$\sigma_{xx}[10^{-3}\sigma_{\mathbb{P}}]$	20.5	17.1	0.96	1.98

geometrical local percolation probabilities correlate surprisingly well with hydraulic permeability and electrical conductivity that determine physical transport.

Acknowledgement

Many of the results discussed in this paper were obtained in earlier cooperations with B. Biswal, C. Manwart, J. Widjajakusuma, P.E. Øren, S. Bakke, and J. Ohser. I am grateful to all of them, and to the Deutsche Forschungsgemeinschaft as well as Statoil A/S Norge for financial support.

References

Adler, P.: 1992, *Porous Media*, Butterworth-Heinemann, Boston.

Bakke, S. and Øren, P.: 1997, 3-d pore-scale modeling of sandstones and flow simulations in pore networks, *SPE J.* **2**, 136.

Barut, A. and Raczka, R.: 1986, *Theory of Group Representations and Applications*, World Scientific, Singapore.

Bear, J.: 1972, *Dynamics of Fluids in Porous Media*, Elsevier Publ. Co., New York.

Bear, J. and Verruijt, A.: 1987, *Modeling Groundwater Flow and Pollution*, Kluwer Academic Publishers, Dordrecht.

Biswal, B., Manwart, C. and Hilfer, R.: 1998, Three-dimensional local porosity analysis of porous media, *Physica A* **255**, 221.

Biswal, B., Manwart, C., Hilfer, R., Bakke, S. and Øren, P.: 1999, Quantitative analysis of experimental and synthetic microstructures for sedimentary rock, *Physica A* **273**, 452.

Bryant, S., Mellor, D. and Cade, C.: 1993, Physically representative network models of transport in porous media, *AIChE J.* **39**, 387.

Chatzis, I. and Dullien, F.: 1977, Modelling pore structure by 2-d and 3-d networks with applications to sandstones, *J. Canad. Petrol. Technol.* page 97. Volume (January–March 1997).

Crivelli-Visconti(ed.), I.: 1998, *ECCM-8 European Conference on Composite Materials*, Woodhead Publishing Ltd, Cambridge.

Delfiner, P.: 1972, A generalization of the concept of size, *J. Microscopy* **95**, 203.

Diebels, S. and Ehlers, W.: 1996, On fundamental concepts of multiphase micropolar materials, *Technische Mechanik* **16**, 77.

Dullien, F.: 1992, *Porous Media – Fluid Transport and Pore Structure*, Academic Press, San Diego.

Ehlers, W.: 1995, Grundlegende Konzepte in der Theorie poröser Medien. Technical report, Institut f. Mechanik, Universität Stuttgart, Germany.

Fatt, I.: 1956, The network model of porous media I. capillary pressure characteristics, *AIME Petroleum Transactions* **207**, 144.

Hadwiger, H.: 1955, *Altes und Neues über konvexe Körper*, Birkhäuser, Basel.

Haslund, E., Hansen, B., Hilfer, R. and Nøst, B.: 1994, Measurement of local porosities and dielectric dispersion for a water saturated porous medium, *J. Appl. Phys.* **76**, 5473.

Hearst, J. and Nelson, P.: 1985, *Well Logging for Physical Properties*, McGraw-Hill, New York.

Hilfer, R.: 1991, Geometric and dielectric characterization of porous media, *Phys. Rev. B* **44**, 60.

Hilfer, R.: 1992, Local porosity theory for flow in porous media, *Phys. Rev. B* **45**, 7115.

Hilfer, R.: 1993, Local porosity theory for electrical and hydrodynamical transport through porous media, *Physica A* **194**, 406.

Hilfer, R.: 1996, Transport and relaxation phenomena in porous media, *Adv. Chem. Phys.* **XCII**, 299.

Hilfer, R., Nøst, B., Haslund, E., Kautzsch, Th., Virgin, B. and Hansen, B. D.: 1994, Local porosity theory for the frequency dependent dielectric function of porous rocks and polymer blends, *Physica A* **207**, 19.

Hilfer, R., Rage, T. and Virgin, B.: 1997, Local percolation probabilities for a natural sandstone, *Physica A* **241**, 105.

Katz, A. and Thompson, A.: 1986, Quantitative prediction of permeability in porous rock, *Phys. Rev. B* **34**, 8179.

Lake, L.: 1989, *Enhanced Oil Recovery*, Prentice Hall, Englewood Cliffs.

Levitz, P. and Tchoubar, D.: 1992, Disordered porous solids: From chord distributions to small angle scattering, *J. Phys. I France* **2**, 771.

Manwart, C. and Hilfer, R.: 1999, (to be published).

Manwart, C., Torquato, S. and Hilfer, R.: 2000, Stochastic reconstruction of sandstones, *Phys. Rev. E* **62**, 893.

Marsily, G.: 1986, *Quantitative Hydrogeology – Groundwater Hydrology for Engineers*, Academic Press, San Diego.

Mecke, K. and Wagner, H.: 1991, Euler characteristic and related measures for random geometric sets, *J. Stat. Phys.* **64**, 843.

Muche, L. and Stoyan, D.: 1992, Contact and chord length distributions of the poisson voronoi tessellation, *J. appl. probab.* **29**, 467.

Quiblier, J.: 1984, A new three dimensional modeling technique for studying porous media, *J. Colloid Interface Sci.* **98**, 84.

Roberts, A.: 1997, Statistical reconstruction of three-dimensional porous media from two-dimensional images, *Phys. Rev. E* **56**, 3203.

Roberts, J. and Schwartz, L.: 1985, Grain consolidation and electrical conductivity in porous media, *Phys. Rev. B* **31**, 5990.

Roy, S. and Tarafdar, S.: 1997, Archies's law from a fractal model for porous rock. *Phys. Rev. B* **55**, 8038.

Sahimi, M.: 1993, Flow phenomena in rocks: From continuum models to fractals, percolation, cellular automata and simulated annealing, *Rev. Mod. Phys.* **65**, 1393.

Sahimi, M.: 1995, *Flow and Transport in Porous Media and Fractured Rock*, VCH Verlagsgesellschaft mbH, Weinheim.

Scheidegger, A.: 1974, *The Physics of Flow Through Porous Media*, University of Toronto Press, Toronto.

Schneider, R.: 1993, *Convex Bodies: The Brunn-Minkowski Theory*, Cambridge University Press, Cambridge.

Schneider, R. and Weil, W.: 1992, *Integralgeometrie*, Teubner, Stuttgart.

Stell, G.: 1985, Mayer-Montroll equations (and some variants) through history for fun and profit. In: M. Shlesinger and G. Weiss (eds), *The Wonderful World of Stochastics*, page 127, Amsterdam, Elsevier.

Stoyan, D., Kendall, W. and Mecke, J.: 1995, *Stochastic Geometry and its Applications*, Akademie-Verlag/Wiley, Berlin/Chichester.

Torquato, S. and Stell, G.: 1982, Microstructure of two phase random media I: The n-point probability functions, *J. Chem. Phys.* **77**, 2071.

Virgin, B., Haslund, E. and Hilfer, R.: 1996, Rescaling relations between two- and three-dimensional local porosity distributions for natural and artificial porous media, *Physica A* **232**, 1.

Widjajakusuma, J., Biswal, B. and Hilfer, R.: 1999a, Quantitative prediction of effective material properties of heterogeneous media, *Comp. Mat. Sci.* **16**, 70.

Widjajakusuma, J., Manwart, C., Biswal, B. and Hilfer, R.: 1999b, Exact and approximate calculations for conductivity of sandstones, *Physica A* **270**, 325.

Yeong, C. and Torquato, S.: 1998, Reconstructing random media, *Phys. Rev. E* **57**, 495.

Ziman, J.: 1982, *Models of Disorder*, Cambridge University Press, Cambridge.