Chapter 6
Summary and Conclusions

Chapter 2

Classical theories of microstructure limitations to transport in porous media (e.g., the Carman-Kozeny equations for flow; Archie's law for conduction) and associated *tortuosity concepts* are reviewed in Chap. 2. These theories were derived a long time ago, when suitable methods for tomography and 3D image analysis were not yet available. The inherent micro–macro relationships are thus based on the consideration of simplified geometry models such as packed beds of mono-sized spheres or parallel tubes. In this way, many aspects of the microstructure could be captured by means of simple morphological descriptors. For example, the wall friction effect and the associated hydraulic radius are described with diameters of spheres or tubes, which are building blocks of simplified microstructure models. Unfortunately, these classical micro–macro relationships with their simplified descriptors cannot easily be transferred to realistic materials with more complex microstructures. Modern adaptations for prediction of effective transport properties in complex microstructures are discussed in Chap. 5.

The *effect of varying path lengths* has been recognized a long time ago as a major microstructure limitation for transport in porous media. Therefore, tortuosity was included as a relevant parameter in the classical theories. However, for practical applications, path lengths and tortuosity are rather complex descriptors, which could not be measured directly from the microstructure until recently. This is one of the reasons why many different definitions, methods and names were introduced in the literature dealing with tortuosity. This multitude of approaches created much confusion, which still nowadays leads to controversial discussions of the topic.

As a countermeasure to this unsatisfactory situation, we propose a *new tortuosity classification scheme*. The classification is based on the selected method, which is used to determine tortuosity (direct versus indirect determination of tortuosities) and

L. Holzer et al., *Tortuosity and Microstructure Effects in Porous Media*,
Springer Series in Materials Science 333,
https://doi.org/10.1007/978-3-031-30477-4_6

on the type of definition (geometric versus physics-based definition of tortuosities). This classification scheme leads to *three main tortuosity categories*:

(a) direct geometric tortuosities
(b) mixed tortuosities
(c) indirect physics-based tortuosities

Based on this classification scheme, we also propose a systematic tortuosity nomenclature, which includes relevant information about the underlying method of determination and details on the geometric or physical definition. The proposed classification scheme and the associated nomenclature are illustrated in Fig. 2.8.

Chapter 3

The relationship between tortuosity and porosity is considered by many authors as a characteristic feature of specific materials classes that can be described with a mathematical expression. To study these relationships, we present an extensive collection of empirical data (tortuosity-porosity couples) from 69 different studies that investigate tortuosity for different materials (appearing in batteries, fuel cells, rocks, packed spheres, fibrous textures, etc.). This collection includes many cases, where different tortuosity types were measured for the same materials. Therefore, these datasets allow a direct comparison of different tortuosity types. This comparison reveals a surprisingly clear picture in the sense that *certain tortuosity types give consistently higher values than others, irrespective of the material under investigation.* With respect to the three main categories of tortuosity, it can be concluded that the measured values for *indirect tortuosities are consistently higher (often >> 2) than those for the mixed and direct tortuosities (often around* $\sqrt{2}$ *and below).* The observed, systematic order among the various tortuosity types is illustrated in Fig. 3.9.

The empirical data furthermore indicates that the measured *values for tortuosity are more strongly dependent on the type of tortuosity than on the material itself*. These findings underline the importance of carefully selecting a suitable method and to precisely declare the corresponding type of tortuosity with the help of the proposed classification scheme and nomenclature.

The empirical data also shows that *tortuosity-porosity couples do not follow a certain trend in general*, but they are scattering within certain limits. In the dilute limit where porosity approaches the value of 1, tortuosity values asymptotically go to 1 as well, which lowers the upper bound of the scattering field. With decreasing porosity, however, the scattering of tortuosity becomes more pronounced as the upper bound increases. For indirect tortuosities, the upper bound is much higher (up to 20 and more for low porosities < 0.3) compared to direct and mixed tortuosities. Therefore, the scattering of indirect tortuosity is stronger. Based on this observation, it must be concluded that *mathematical expressions for tortuosity-porosity relationships (e.g., the Bruggeman relation) cannot have any universal meaning*. Mathematical tortuosity-porosity formulas can thus only be meaningful when they are derived for a specific tortuosity type and for special microstructure variations, which are discussed in the present paper. Hence, from a generalized point of view, there is much evidence that microstructure characteristics, such as tortuosity, porosity, constrictivity and pore size, can vary independently of each other (within a certain range). In order to describe microstructure effects properly it is therefore necessary to find suitable characterization techniques for all relevant microstructure characteristics.

Chapter 4

An extensive overview of methodologies is given for microstructure characterization in general, and for tortuosity analysis in particular. The workflow for a thorough 3D characterization (see Fig. 4.1) includes several methodologies that are rapidly evolving. Each of these methodologies is reviewed specifically:

(a) tomography
(b) qualitative image processing (3D reconstruction, filtering, and segmentation)
(c) quantitative image analysis (specific algorithms for each tortuosity type)
(d) numerical simulation of transport (conduction, diffusion, flow)
(e) stochastic microstructure modeling and virtual materials testing.

In particular, the different *calculation approaches for the three main tortuosity categories are discussed separately*: The computation of *direct geometric tortuosities* is based on quantitative 3D image analysis. The *indirect physics-based tortuosities* are computed from effective properties, which are determined by numerical transport simulations (or by real laboratory experiments). For *mixed tortuosities*, volume fields obtained by numerical transport simulation are used. The mixed tortuosities are then computed by geometric analysis of these volume fields (i.e., 3D image analysis of streamlines or velocity vectors). Hence, the mixed tortuosities contain information that covers physics-based as well as geometric aspects. In this sense, the *mixed tortuosities can be considered as the most advanced and most relevant descriptors for the path length effect.* For practical help, an *extensive list with available SW packages* and codes for microstructure analysis and modeling is presented (see Table 4.6), with a special emphasize on tortuosity characterization.

Chapter 5

Based on the methodological progress in tomography, 3D image analysis, stochastic microstructure modeling, artificial intelligence and virtual materials testing, new possibilities become available, which allow a thorough characterization of microstructures at different length scales and with different complexities. Investigations using combinations of these modern methodologies provide a *better understanding of the underlying micro–macro relationships.* A prerequisite for these improvements is *better descriptors for the path length effect by means of direct geometric and mixed tortuosities. But also for the bottleneck effect and for the wall friction effect, improved descriptors could be found, such as constrictivity and hydraulic radius* based on MIP-PSD and cPSD. In Chap. 5, it is summarized how these new descriptors were used to establish *new quantitative micro–macro relationships.* Typically, recent approaches are data-driven, and, for this purpose, they involve methods of stochastic geometry, machine learning, virtual materials testing and error minimization. (References to a series of relevant studies in this field are given in Chap. 5).

For conduction and diffusion, the evolution of the most important formulas describing micro–macro relationships is summarized in Fig. 5.1. From the numerous equations that were evaluated, Eq. 5.2b, i.e.,

$$M_{pred} = \varepsilon^{1.15} \beta^{0.37} / \tau_{dir\_geodesic}^{4.39}, \tag{5.2b}$$

has the highest overall prediction power with a MAPE of 19.06% (Note: the precision power drops for materials with M > 0.7). Thereby, M_{pred} is equivalent to the relative electric conductivity (σ_{ele_rel}) and/or relative diffusivity (D_{rel}). It must be emphasized that for microstructures with a high porosity, more precise predictions are obtained by Eq. 5.8b, i.e.,

$$M_{pred} = \varepsilon^{1.67-0.48\beta} / \tau_{dir\_geodesic}^{5.18}, \tag{5.8b}$$

with a $\text{MAPE}_{\text{total}}$ of 18.3% (and a MAPE of 10.3% for microstructures with M > 0.05).

For viscous flow in porous media, the evolution of micro–macro formulas is summarized in Fig. 5.2. Two different expressions for permeability (κ_I, κ_{II}) are derived, namely Eq. 5.37, i.e.,

$$\kappa_I = 0.54 \left(\frac{\varepsilon}{S_V} \right)^2 \frac{\varepsilon^{3.56} \beta^{0.78}}{\tau_{dir\_geodesic}^{1.67}}, \tag{5.37}$$

with a MAPE of 34.5%, and Eq. 5.40, i.e.,

$$\kappa_{II} = \frac{(0.94 r_{min} + 0.06 r_{max})^2}{8} \frac{\varepsilon^{2.14}}{\tau_{dir\_geodesic}^{2.44}}, \tag{5.40}$$

with a MAPE of 34.54%. Thus, both formulas have almost the same prediction powers. Moreover, compared to classical theories such as the Carman-Kozeny equation for flow and Archie's low for conduction, these new micro–macro relationships have a much higher prediction power. In particular, they can also be used for complex disordered microstructures, where the classical theories mentioned above are not applicable. These improvements are mainly due to the progress of recent 3D methodologies, which provide better morphological descriptors.

Interpretation of the three main tortuosity categories

Nowadays many different possibilities are available for the characterization of tortuosity. In this context the findings from the *review of empirical data* (Chap. 3) must be kept in mind. Thereby *a consistent pattern is observed, which indicates that the measured values of tortuosity are more strongly dependent on the tortuosity type (and* *on the associated method) than on the material itself.* It is thus important to understand the differences between specific tortuosity types. Which type of tortuosity and which calculation approach one should choose, depends on the information that is required for a specific purpose. The basic arguments for different tortuosity classes can be summarized as follows:

(a) *Indirect physics-based tortuosities* describe *bulk resistances of the microstructure* against specific transport processes. They do not contain strict geometric information and therefore they do not really contribute to a fundamental understanding of the path length effect. Indirect tortuosities are *lumped parameters, which include not only the limiting effect of paths lengths variations but also other microstructure limitations such as the bottleneck effects.* Indirect tortuosities are often used as input for macro-homogeneous models. For this purpose, they are well suited, since they describe the bulk resistive influence of the microstructure.

(b) *Direct geometric tortuosities* are based on *measurements of path lengths* through the 3D microstructure. For materials engineers, the geometric tortuosity reveals morphological information that is relevant for purposeful microstructure optimization. However, microstructure limitations on transport cannot be fully described by the geometric tortuosity alone. In order to understand the relationship between microstructure and effective transport properties, *it is necessary to consider additional microstructure characteristics, such as constrictivity, porosity and hydraulic radius.* In context with new micro–macro formulas (e.g., Eq. 5.2b), the *geodesic tortuosity* turns out to be a suitable geometric descriptor for path-length effects. However, since the geometric tortuosities are *not physics-based*, this leaves some room for further improvement of micro–macro formulas and their prediction power.

(c) *Mixed tortuosities* include the *advantages of both calculation approaches*, in the sense that they contain *true information of the path lengths (i.e., geometric)* and at the same time, they are *specific for the underlying transport process (i.e., physics-based).* Mixed tortuosities thus bear key information that is necessary to understand path length effects of specific transport mechanisms on a fundamental level. It is thus probable that the prediction power of modern micro–macro relationships (such as Eq. 5.2b and Eq. 5.37) can be further improved in future by using mixed tortuosities as descriptors for the paths length effect.