

# Critical review of the impact of tortuosity on diffusion

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## Abstract

Most of the present formulations for the mass conservation of species do not correctly represent changes in the time scale of diffusion as a function of porosity in a system of porous media. In sediments, or in any porous system, the presence of solid particles causes the diffusion paths of species to deviate from straight lines. To represent the role of porosity on diffusion, the diffusion coefficient must be scaled with tortuosity. In this paper we present a review of the available formulations for the scaled diffusion coefficient with tortuosity, sensitivity tests with analytical solutions, and calibration of these formulations with respect to measured data.

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## 1. Introduction

In general, transport by advection dominates in zones of high permeability (or hydraulic conductivity) of a porous medium, such as fractures, while diffusion dominates in zones of low permeability, such as clay layers. To predict the fate and transport of species (e.g., solutes), a detailed understanding of diffusion processes is crucial. The use of Fick's first law to model diffusion fluxes is arguably the most common and important method in groundwater hydrology and petroleum reservoirs. However, most of the present models for these fluxes do not correctly represent changes in the time scale of diffusion as a function of porosity in a system of porous media (Aziz and Settari, 1979; Chen et al., 2006; Helmig, 1997).

In sediments, or in any porous system, the presence of solid particles causes the diffusion paths of species to deviate from straight lines. To represent the role of porosity on diffusion,

the diffusion coefficient must be scaled with tortuosity (van Cappellen and Gaillard, 1996). Attempts have been made to incorporate tortuosity using experimental, theoretical, and empirical approaches.

There exist at least two experimental approaches that lead to an indirect estimate of tortuosity. One approach measures the diffusion coefficient of a chosen nonreactive species both in free solution and in a sediment of known porosity (Sweerts et al., 1991), which is a time-consuming process. The other approach relates the tortuosity to a measured quantity termed the formation factor that is obtained from electrical resistivity measurements (McDuff and Ellis, 1979). However, calculation of this factor requires specialized equipment (resistivity probes).

Theoretical approaches are based on a certain model of the structure of a porous medium. They have the advantage that they generally do not contain any adjustable parameter, but theoretical models are highly idealized. The simplest of such models is a collection of randomly oriented capillaries cutting through a solid body (Bhatia, 1985; Dykhuizen and Casey, 1989; Petersen, 1958).

Empirical models resemble the theoretical models, but contain adjustable parameters. These parameters depend on the pore geometry, and their reported values in literature vary

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significantly. It appears that Archie's law was the first used in the description of such a model (Archie, 1942). There have been various attempts to give theoretical derivations of this law, but none has been found to be theoretically sound.

In this paper we present a review of theoretical and empirical models that incorporate tortuosity in the diffusion coefficient. We also give sensitivity tests with analytical solutions for these models, and their calibration with respect to measured data. In the next section, we briefly review transport equations that are often used in predicting the fate and transport of species in porous media, and point out their shortcomings. Then, in the third section we review theoretical and empirical models that describe the impact of tortuosity on the diffusion coefficient. We conclude with some remarks in the final section.

## 2. Diffusive transport

We consider the transport of a species (e.g., a solute) in a fluid phase that occupies the entire void space in a porous medium. We do not consider the effects of chemical reactions between the species in the fluid phase, radioactive decay, biodegradation, and growth due to bacterial activities that cause the quantity of this species to increase or decrease. Conservation of mass of the species in the fluid phase is given by Bear (1972) and Chen et al. (2006)

$$\frac{\partial(\phi c \rho)}{\partial t} = -\nabla \cdot (c \rho \mathbf{u} - \rho \mathbf{D} \nabla c) + q, \quad (2.1)$$

where  $\phi$  is the porosity of the porous medium (the fraction of a representative elementary volume available for the fluid),  $\rho$  is the density of the fluid per unit volume,  $\mathbf{u}$  is the Darcy velocity of the fluid,  $c$  is the concentration (volumetric fraction in the fluid phase) of the species,  $\mathbf{D}$  is the diffusion–dispersion tensor, and  $q$  is the source/sink term. Darcy's law for the fluid is expressed as

$$\mathbf{u} = -\frac{1}{\mu} \mathbf{k}(\nabla p - \rho g \nabla z), \quad (2.2)$$

where  $p$  is the fluid pressure,  $\mathbf{k}$  is the absolute permeability tensor of the porous medium,  $\mu$  is the fluid viscosity,  $g$  is the magnitude of the gravitational acceleration, and  $z$  is the depth.

The diffusion–dispersion tensor  $\mathbf{D}$  in (2.1) in three space dimensions is defined by

$$\mathbf{D}(\mathbf{u}) = \phi \{ d_m \mathbf{I} + |\mathbf{u}| (d_l \mathbf{E}(\mathbf{u}) + d_t \mathbf{E}^\perp(\mathbf{u})) \}, \quad (2.3)$$

where  $\mathbf{I}$  is the identity tensor,  $d_m$  is the molecular diffusion coefficient,  $d_l$  and  $d_t$  are, respectively, the longitudinal and transverse dispersion coefficients,  $|\mathbf{u}|$  is the Euclidean norm of  $\mathbf{u} = (u_1, u_2, u_3)$ :  $|\mathbf{u}| = \sqrt{u_1^2 + u_2^2 + u_3^2}$ ,  $\mathbf{E}(\mathbf{u})$  is the orthogonal projection along the velocity:

$$\mathbf{E}(\mathbf{u}) = \frac{1}{|\mathbf{u}|^2} \begin{pmatrix} u_1^2 & u_1 u_2 & u_1 u_3 \\ u_2 u_1 & u_2^2 & u_2 u_3 \\ u_3 u_1 & u_3 u_2 & u_3^2 \end{pmatrix},$$

and  $\mathbf{E}^\perp(\mathbf{u}) = \mathbf{I} - \mathbf{E}(\mathbf{u})$ . While the tensor dispersion may be physically more important than the molecular diffusion in some cases, we focus our study only on the diffusion in this paper.

We consider a scenario where the species only diffuse within a constant density fluid in a homogeneous porous medium without a source or sink. In this case, it follows from (2.1) without dispersion that the conservation equation becomes

$$\frac{\partial c}{\partial t} = d_m \Delta c. \quad (2.4)$$

As anticipated by the evaluation of the governing equation, the solution of (2.4) does not depend on porosity since diffusion time and length scales are not functions of the porosity. This implies that the concentrations will be identical when the user stipulates 0% or 100% porosity, an incorrect result. To represent the role of porosity on ordinary molecular diffusion, the diffusion coefficient must be scaled with tortuosity.

## 3. Impact of tortuosity on diffusion

As noted earlier, in sediments, or in any porous system, the presence of solid particles causes the diffusion paths of species to deviate from straight lines (see Fig. 1). Consequently, the diffusion coefficients of species must be corrected for the tortuosity. Both theory and dimensional reasoning (Petersen, 1958; Ullman and Aller, 1982; van Brakel and Heertjes, 1974) suggest that the diffusion coefficient be scaled with tortuosity  $\tau$  as follows:

$$d'_m = \frac{d_m}{\tau^2}, \quad (3.1)$$

where  $d_m$  is now the diffusion coefficient of the species in question in the fluid (e.g., water) without the presence of the sediment matrix. Relations other than (3.1) will be discussed later in Section 3.4.

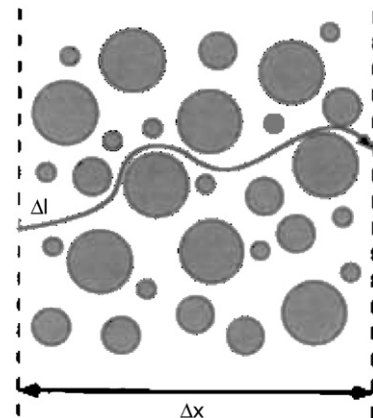


Fig. 1. Convolute diffusion path in a sediment from Boudreau (1996).

### 3.1. Theoretical relations

The general requirements for the tortuosity  $\tau$  are (Boudreau, 1996): first,

$$\tau^2 \geq 1, \quad (3.2)$$

which simply means that the actual (average) path traversed by the species while diffusing in the interstitial fluid in a porous medium is longer than in the absence of the solid. Second,

$$\lim_{\phi \rightarrow 1} \tau = 1; \quad (3.3)$$

that is, there is no hindrance to diffusion in the absence of any (impermeable) solid. Finally,  $\tau \rightarrow \infty$  if and only if  $\phi \rightarrow 0$ ; i.e., the tortuosity is finite for all nonzero values of porosity, so hindrance is complete only if the pore-space disappears. This property skips the important topic of connectivity at low porosity.

Physically, tortuosity is defined as the ratio of the actual distance  $\Delta l$  travelled by the species per unit length  $\Delta x$  of the medium (see Fig. 1):

$$\tau = \frac{\Delta l}{\Delta x}. \quad (3.4)$$

It is sometimes defined by the square of this ratio (Dullien, 1979), which and (3.4) will lead to an equivalent diffusion coefficient (see Section 3.4). Unlike  $\phi$ , the parameter  $\tau$  cannot be measured directly. The literature contains both theoretical and empirical relations for evaluating  $\tau$ . As noted, theoretical relations are based on a certain model of the structure of a porous medium. They have the advantage that they generally do not contain any adjustable parameter, but these relations are highly idealized. The simplest of such models is a collection of randomly oriented capillaries cutting through a solid body. Different treatments of the capillary model yield (Petersen, 1958)

$$\tau = \sqrt{2}, \quad (3.5)$$

or (Bhatia, 1985; Dykhuizen and Casey, 1989)

$$\tau = \sqrt{3}. \quad (3.6)$$

Experimental values of  $\tau$  can be either smaller or larger than these numerical values (see Figs. 2–4). In fact, its measured values correlate with  $\phi$  (Archie, 1942; van Brakel and Heertjes, 1974), which suggests that theoretical models for  $\tau$  depend on  $\phi$ .

Table 1 is a collection of theoretical tortuosity–porosity relations that satisfy the above three requirements, with remarks on the physical system on which each relation is based. The important point here is whether these relations are useful in calibrating observed sedimentary tortuosity data. The data have been measured from various marine and lacustrine sediments (Archer et al., 1989; Goldhaber et al., 1977; Jorgensen, 1978; Krom and Berner, 1980; Li and Gregory, 1974; Manheim and Waterman, 1974; Sweerts et al., 1991; Ullman and Aller, 1982). Since the data given in Iversen and Jorgensen (1993) and Sweerts et al.

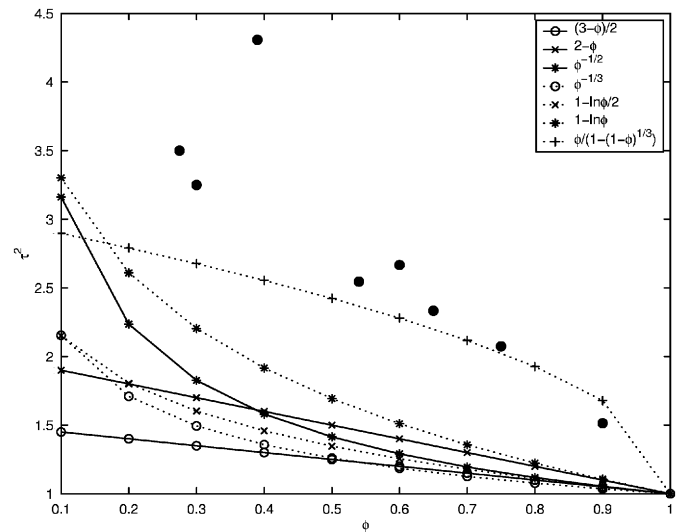


Fig. 2. Plot of the first eight theoretical tortuosity–porosity relations in Table 1 against the measured data from Iversen and Jorgensen (1993).

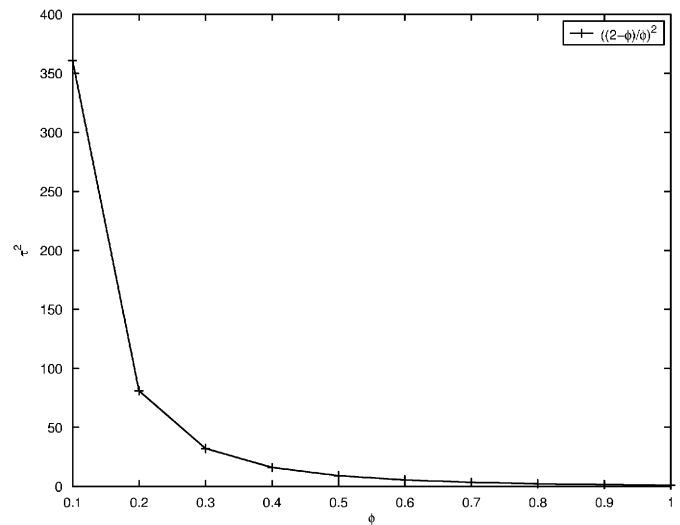


Fig. 3. Plot of the last theoretical tortuosity–porosity relation in Table 1.

(1991) are well represented for the fine-grained marine and lacustrine sediments, respectively, as examples we plot the theoretical relations given in Table 1 against these two sets of data.

In Iversen and Jorgensen (1993) the tracer diffusion coefficients of sulfate and methane were determined in seawater, with sediments collected along the Danish coast. At water depth varying from 50 cm to 200 m, the sediment composition varied from sandy sediments to fine-grained silt and clay, with the majority of the samples from silt–clay types. A set of cores was collected from the bottom of clay beach dunes. This station cannot be classified as marine sediments, but the dune is raised sea-bottom, and the clay was in contact with seawater and closely resembled consolidated marine. The tracer diffusion measurement method in Iversen and Jorgensen (1993) was based on the instantaneous source technique (Duursma and Bosch, 1970); that is, the solution to the one-dimensional

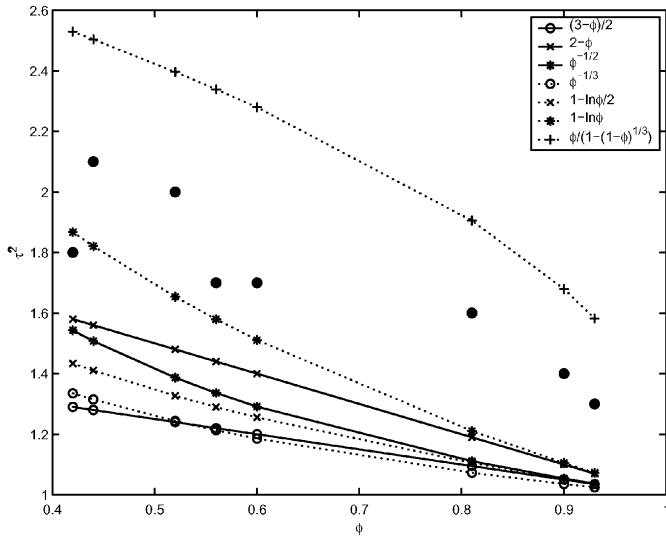


Fig. 4. Plot of the first eight theoretical tortuosity–porosity relations in Table 1 against the measured data from Sweerts et al. (1991).

counterpart of equation (2.4) with an instantaneous source was used to calculate the tracer diffusion coefficients.

Figs. 2 and 3 plot the theoretical relations in Table 1 against the data from Iversen and Jørgensen (1993) (because of a great scale difference, the first eight relations are plotted in Fig. 2, while the last one in Table 1 is plotted in Fig. 3). These two plots indicate that none of the theoretical relations in Table 1 adequately match the measured data from Iversen and Jørgensen (1993).

We now plot the theoretical relations in Table 1 against the data for lacustrine sediments taken from Sweerts et al. (1991); see Fig. 4. In Sweerts et al. (1991) the whole-sediment molecular diffusion coefficients for tritiated water in pore waters of various lakes were determined experimentally by adding  $^3\text{H}_2\text{O}$  to the overlying water of asphyxiated (without bioirrigation) and unasphyxiated cores and measuring the resulting pore-water profiles after a period of time. The measurement method used a constant-source computer model that was based on the error function technique (Duursma and Hoede, 1967).

All the plots in Figs. 2–4 show that none of the theoretical relations in Table 1 accurately match the measured data. The problem is that these relations are based on mathematically idealized geometries (e.g., spherical or rectangular packings of some type, as shown in Table 1) of real sedimentary fabrics.

### 3.2. Empirical relations

As shown above, the theoretical relations do not match the data that describe sediments of very different types. Empirical relations that contain adjustable parameters are analogous to the theoretical ones but describe better the observed data.

Experimentally, the tortuosity of a sediment can be obtained by measuring the porosity  $\phi$  and the formation resistivity factor  $F$ , as noted earlier. These three variables are related by

$$\tau^2 = (F\phi)^n, \quad (3.7)$$

where  $n$  is an adjustable empirical parameter. The formation factor  $F$  is determined by measuring the resistivity of a porous medium, relative to that of the free solution. Microelectrode technology currently leads to fine-scale profiles of this factor in surface sediments (van Cappellen and Gaillard, 1996). However, this information is hardly available and must rely on an empirical relation that relates  $F$  to the sediment porosity  $\phi$ . Following Faris et al. (1954) and Nelson and Simmons (1995), this relation is usually described by Archie's (1942) law:

$$F = \frac{A}{\phi^m}, \quad (3.8)$$

where  $A$  and  $m$  are empirical parameters. Substituting (3.7) into (3.8) gives the relation of tortuosity in terms of porosity:

$$\tau^2 = (A\phi^{1-m})^n, \quad (3.9)$$

with three adjustable parameters  $A$ ,  $m$ , and  $n$ . These parameters are lithology-dependent. Relation (3.9) was used for sands (Lerman, 1979) and muds (Ullman and Aller, 1982) with  $A = n = 1$  (also see Boudreau, 1996; van Cappellen and Gaillard, 1996 for the same choice of these parameters).

There are other types of empirical relations such as the linear function (Iversen and Jørgensen, 1993; Low, 1981)

$$\tau^2 = \phi + B(1 - \phi), \quad (3.10)$$

and the logarithmic function (Boudreau, 1996; Weissberg, 1963)

$$\tau^2 = 1 - C \ln \phi, \quad (3.11)$$

where  $B$  and  $C$  are adjustable parameters. These three types of empirical relations are summarized in Table 2.

Note that (3.10) with  $B = 0$  becomes (3.9) with  $A = n = 1$  and  $m = 0$ . Also, with  $C = 2$  (Boudreau, 1996), relation (3.11) becomes

$$\tau^2 = 1 - 2 \ln \phi = 1 + \ln \left( \frac{1}{\phi^2} \right),$$

which can be expanded in the series of the logarithm about the value  $\phi^{-2} = 1$  (i.e.,  $\phi = 1$ ):

$$\tau^2 = 1 + \left( \frac{1}{\phi^2} - 1 \right) - \frac{1}{2} \left( \frac{1}{\phi^2} - 1 \right)^2 + \frac{1}{3} \left( \frac{1}{\phi^2} - 1 \right)^3 - \dots$$

For values of  $\phi$  near 1, only the second term in the right-hand side is significant, so

$$\tau^2 \approx 1 + \left( \frac{1}{\phi^2} - 1 \right) = \frac{1}{\phi^2},$$

which corresponds to (3.9) with  $A = n = 1$  and  $m = 3$ . This case was investigated in Ullman and Aller (1982) where a  $\phi^{-3}$ -dependence for the formation factor  $F$  was necessary to explain high porosity data.

Figs. 5 and 6 show the best least-squares fits of relations (3.9)–(3.11) to the same sets of data as given in Figs. 2 and 4, and Table 3 lists the corresponding parameter values and the

Table 1  
Theoretical tortuosity–porosity relations, their physical systems, and references

Relations	Remarks	References
$\tau^2 = (3 - \phi)/2$	Ordered packings	Akanni et al. (1987) and Maxwell (1881)
$\tau^2 = (3 - \phi)/2$	Random homogeneous isotropic sphere packings	Neale and Nader (1973)
$\tau^2 = 2 - \phi$	A hyperbola of revolution	Petersen (1958) and Rayleigh (1892)
$\tau^2 = \phi^{-1/2}$	Not for monosized spheres	Bruggemann (1935)
$\tau^2 = \phi^{-1/3}$	Partly saturated homogeneous isotropic monodisperse sphere packings	Millington (1959) and van Brakel and Heertjes (1974)
$\tau^2 = 1 - \ln \phi/2$	Overlapping spheres	Akanni et al. (1987), Ho and Strieder (1981), van Brakel and Heertjes (1974) and Weissberg (1963)
$\tau^2 = 1 - \ln \phi$	Random arrays of freely overlapping cylinders	Tomadakis and Sotirchos (1983)
$\tau^2 = \phi/(1 - (1 - \phi)^{1/3})$	Heterogeneous catalyst	Beekman (1990)
$\tau^2 = ((2 - \phi)/\phi)^2$	Cation-exchange resin membrane	Mackie and Meares (1955)

Table 2  
Empirical tortuosity–porosity relations, their physical systems, and references

Relations	Adjustable parameters	Remarks	References
$\tau^2 = (A\phi^{1-m})^n$	$A, m, \text{ and } n$	Sands, muds	Lerman (1979) and Ullman and Aller (1982)
$\tau^2 = \phi + B(1 - \phi)$	$B$	Soils, catalysts	Iversen and Jorgensen (1993) and Low (1981)
$\tau^2 = 1 - C \ln \phi$	$C$	Fine-grained un lithified sediments	Boudreau (1996) and Weissberg (1963)

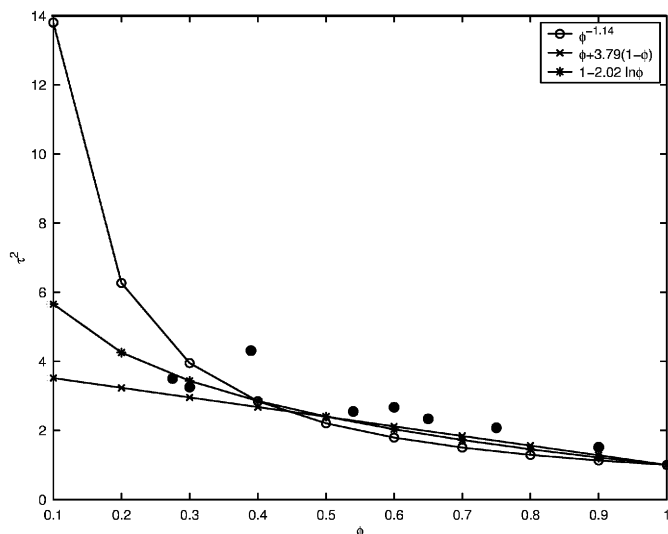


Fig. 5. Plot of the empirical tortuosity–porosity relations in Table 3 against the measured data from Iversen and Jorgensen (1993).

statistics of these fits. The measured data from Iversen and Jorgensen (1993) were given only for  $\phi \geq 0.275$ . In Fig. 5, for completeness we plot the three relations for  $\phi$  in the interval  $[0.1, 1.0]$ . All these three relations provide statistically significant correlations to the data in excess of 50% of the variance for  $\phi \geq 0.275$ . The latter two relations seem to give better fits than the first one. This can be also seen from Fig. 6 where the measured data from Sweerts et al. (1991) were given only for  $\phi \geq 0.4$ .

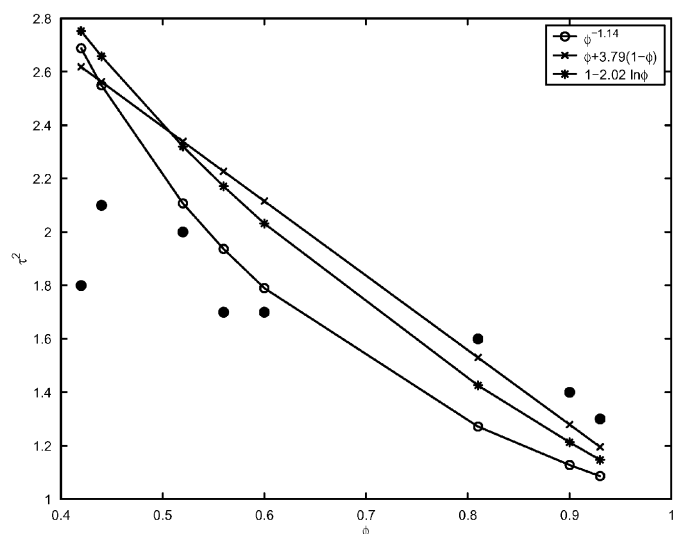


Fig. 6. Plot of the empirical tortuosity–porosity relations in Table 3 against the measured data from Sweerts et al. (1991).

The default values in equation (3.9) can be chosen as follows:

$$A = 1, \quad m = 2, \quad n = 1. \quad (3.12)$$

The tortuosity–porosity relations given in Boudreau (1996), Boving and Grathwohl (2001) and Low (1981), together with relation (3.9) with these default values, are plotted in Fig. 7. These relations seem matching well for  $\phi \geq 0.4$ .

Table 3  
Best least-squares fits for the empirical relations (3.9)–(3.11)

Relations	Parameter values	$r^2$ (variance)
$\tau^2 = (A\phi^{1-m})^n$	$A = n = 1$ and $m = 2.14 \pm 0.02$	0.54
$\tau^2 = \phi + B(1 - \phi)$	$B = 3.79 \pm 0.10$	0.63
$\tau^2 = 1 - C \ln \phi$	$C = 2.02 \pm 0.09$	0.64

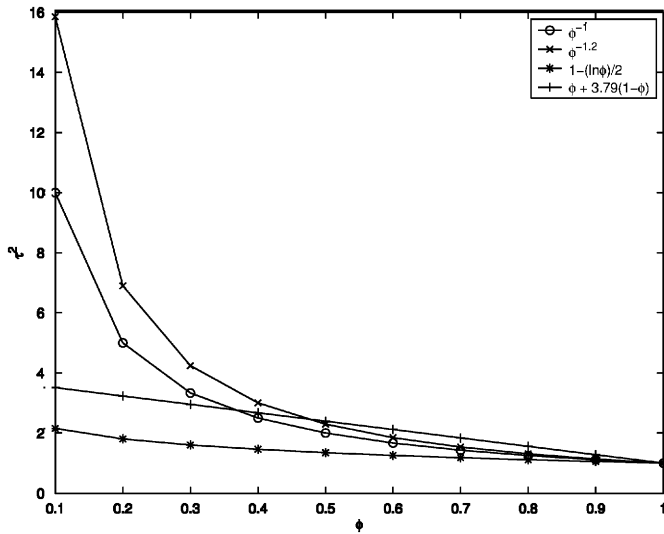


Fig. 7. Plot of the empirical tortuosity–porosity relations in Boudreau (1996), Boving and Grathwohl (2001) and Low (1981) and relation (3.9) with default values in (3.12).

### 3.3. Sensitivity analysis

We now consider the same problem as at the end of the previous section. With a scaled diffusion coefficient (see equation (3.1)), the diffusion problem (2.4) now becomes

$$\frac{\partial c}{\partial t} = \frac{d_m}{\tau^2} \Delta c, \tag{3.13}$$

which we solve on a square domain. The boundary conditions on the east and west boundaries are of the homogeneous Dirichlet-type (i.e.,  $c = 0$ ) and are of no flow-type on the top and bottom (i.e.,  $\partial c / \partial \mathbf{n} = 0$ , where  $\mathbf{n}$  is the unit normal outward to the square domain). The initial condition is  $c = 1$ , and we choose  $d_m = 0.02$  and  $\tau^2$  given by Eq. (3.9) with the default values in (3.12). The analytical solution to (3.13) demonstrates the sensitivity of diffusivity to the tortuosity defined by (3.9); see Fig. 8, where the final time is  $T = 5000$  s and the increment from  $\phi = 0.05$  to 0.5 is 0.05. Unlike (2.4), Eq. (3.13) now produces a physically reasonable solution.

### 3.4. Remarks on the impact of tortuosity on diffusion

There are essentially two classes of definitions for the scaled diffusion coefficient  $d'_m$ . The first class follows Eq. (3.1) (Berner, 1980; Maerki et al., 2004), with the tortuosity  $\tau$  given by (3.4). In Andrews and Bennett (1981), Boudreau

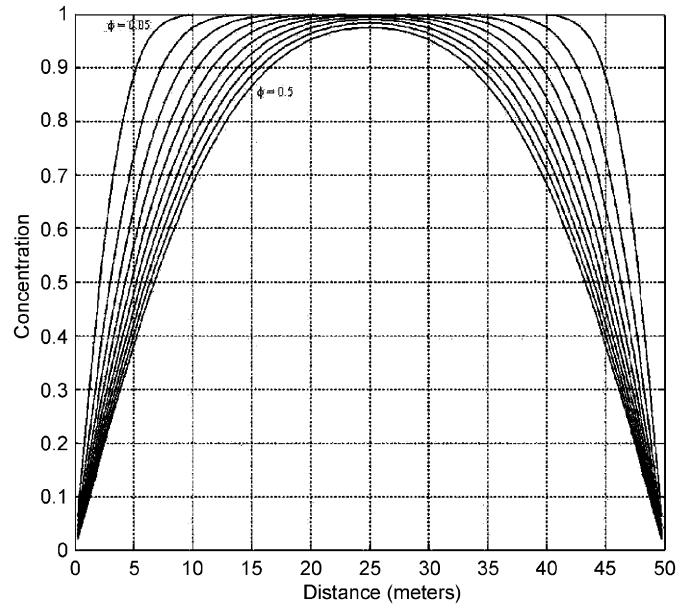


Fig. 8. Sensitivity of diffusion to the tortuosity (dependence of the solution to Eq. (3.13) on  $\phi$ ).

(1996) and McDuff and Ellis (1979), the tortuosity is given by  $\tau^2 = F\phi$ , which corresponds to Eq. (3.7) with  $n = 1$ .

The second class defines the scaled diffusion coefficient as follows (Aris, 1975; Dullien, 1979; Shackelford, 1991; Sherwood et al., 1975; Thomas, 1989):

$$d'_m = \frac{d_m}{\tau}, \tag{3.14}$$

with the tortuosity  $\tau$  given by

$$\tau = \left( \frac{\Delta l}{\Delta x} \right)^2. \tag{3.15}$$

We can easily see that the two definitions, (3.1) with (3.4) and (3.14) with (3.15), are equivalent.

In addition to the definitions (3.1) and (3.14), there exist other definitions for  $d'_m$ . In Popovičová and Brusseau (1997), the tortuosity  $\tau$  in Eq. (3.14) is given by

$$\tau = \phi^{-2/3}.$$

Also, in Sherwood et al. (1975) it is defined by

$$d'_m = \frac{d_m \phi}{\tau}. \tag{3.16}$$

Finally, the scaled diffusion coefficient  $d'_m$  in Boving and Grathwohl (2001) is defined as, with  $\tau$  given by (3.15),

$$d'_m = \frac{d_m \phi \delta}{\tau}, \tag{3.17}$$

where  $\delta$  is the “constrictivity”—a dimensionless variable that becomes important if the size of the species becomes comparable to the size of the pore.

#### 4. Conclusions

In this paper we have presented a review of theoretical and empirical models that incorporate tortuosity in the diffusion coefficient. We have also given sensitivity tests with analytical solutions of these models, and their calibration with respect to measured data. The focus of our study is on the ordinary molecular diffusion. That is, the diffusion–dispersion tensor  $\mathbf{D}$  in (2.3) is adjusted to

$$\mathbf{D}(\mathbf{u}) = \phi \left\{ \frac{d_m}{\tau^2} \mathbf{I} + |\mathbf{u}| (d_l \mathbf{E}(\mathbf{u}) + d_t \mathbf{E}^\perp(\mathbf{u})) \right\}. \quad (4.1)$$

Now, the question arises: Should the inverse relationship with tortuosity be also multiplied with the dispersion terms? Keeping it separate is motivated by the existing papers. Since the dispersion coefficients are also empirical, however, where the inverse relationship is placed would depend on how the dispersion coefficients are measured. Future research is needed to determine how the tortuosity affects dispersion. We end with a remark that while porous media characteristics such as grain size, shape, and coordination numbers impact diffusion coefficients, our study focuses on various theoretical and empirical relations for tortuosity.

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