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Connection between electrical conductivity and diffusion coefficient of a conductive porous material filled with electrolyte.

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Abstract. The paper focuses on the cross-property connection between the effective electrical conductivity and the overall mass transfer coefficient of a two phase material. The two properties are expressed in terms of the tortuosity parameter which generalized to the case of a material with two conductive phases. Elimination of this parameter yields the cross-property connection. The theoretical derivation is verified by comparison with computer simulation.

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1. Introduction.

The practical implementation of homogenization schemes to calculate the overall properties of heterogeneous materials often requires information that is not available. The accurate predictions are based on the knowledge of the properties of constituents, relative volume functions, and parameters characterizing the мицроструцтуре. While material properties of the constituents and their volume fractions are generally known, information about morphology of the material may be incomplete or inappropriate. This information, however, may be reconstructed by measuring the set of properties different from ones of interest and using cross-property connections.

Existence of cross-property connections has been recognized first from the observations of qualitative nature. For instance, geophysicists noticed that cracks in rocks increase both the elastic compliance and the fluid permeability; in fracture mechanics, attempts have been made to relate the loss of elastic stiffness of a deteriorating microstructure to lifetime predictions. Quantitative theoretical results on cross-property connections started to appear in 1950's. In works of Wyllie and Rose (1950), Klinkenberg (1951), and Wyllie and Spangler (1952) method of evaluation of hydraulic conductivity of porous rock through electrical conductivity measurements has been developed. Pores were filled with electrolyte and the solid skeleton of the porous material was considered as a perfect electrical insulator impenetrable for the liquid. Bristow (1960) derived explicit connection between elastic constants and electrical conductivity for a material containing multiple randomly crack orientated cracks. Levin (1967) interrelated the effective bulk modulus and the effective thermal expansion coefficient of a two phase isotropic composite. Prager (1969) constructed Hashin-Shtrikman-based bounds for the effective magnetic permeability (or electrical conductivity) in terms of the effective thermal conductivity of a two-phase isotropic material. Later, many results have been obtained on correlation between linear elastic and conductive (thermal or electrical) properties of heterogeneous materials. Cross-property bounds have been obtained by Milton (1984) and Gibiansky and Torquato (1995, 1996 a,b); explicit approximate connections have been derived by Sevostianov and Kachanov (2002) (see also Sevostianov, 2003; and review Sevostianov and Kachanov, 2009). Exact connections between normal compliance and spreading resistance of two contacting surfaces have been developed by Barber (2003), Sevostianov and Kachanov (2004) and Sevostianov (2010). Connections between electrical conductivity and fluid permeability of a porous material have been developed by Torquato (1990) and Avellaneda and Torquato (1991) under assumption that the solid skeleton does not conduct electricity and the physical properties are refer to the porous space filled with electrolyte (such a situation is typical, for example, for geophysical applications). *Generally speaking, cross-property connections can be developed if microstructural parameters controlling two physical properties are either the same or similar* (see review of Sevostianov and Kachanov, 2009).

Another possibility appears when the properties of interest are governed by *supplemental parameters*, like in the case of elastic properties and electrical conductivity of saturated rock, where the latter is determined by microgeometry of the porous space and elastic properties are controlled by the morphology of the solid phase. Berryman and Milton (1988) derived variational cross-property bound for such a case. Sevostianov and Shrestha (2010), using results of Sevostianova et al (2010), derived connections between fluid permeability of a porous material and electrical conductivity through the solid skeleton. They developed variational bounds and explicit closed-form connection between the two physical properties. Their results were numerically verified by Garsia and Sevostianov (2012)

In the present paper, we consider a porous material with electrically conductive skeleton. The pores are assumed to be filled with electrically conductive liquid. Diffusion of a substance of interests is possible in the liquid as well as in the skeleton. The paper focuses on the problem of the evaluation of the overall mass transfer coefficient of such a material from the electrical conductivity measurements. The derivation is based on the elimination of the microstructural parameter – tortuosity of the porous space – that governs both the properties. Analytical derivations are compared with FEM calculations.

2. Tortuosity as a microstructural parameter in the context of mass transfer and electrical conductivity: the concept and the history of terminology.

The electrical and mass transport performances of any porous material are strongly dependent on their three-dimensional (3D) microstructures, which include the porosity, pore sizes and shapes and connectivity of the porous space. These microstructural parameters can be collectively described as the "tortuosity of the porous space" (see, for example, Chen et al, 2013).

The term tortuosity, to the best of our knowledge, has been first introduced by Thomson and Tait (1879) in the context of curvature of a non-plane curve (see Sections 7- 9 of their book). Noting $\delta\phi$ the angle between the osculating planes at two points at a distance δs from one another along the curve, they defined tortuosity τ of a curve as a derivative

$$\tau_{T-T} = \frac{d\phi}{ds} \tag{2.1}$$

(we use subscript "T-T" to identify definition of Thomson and Tait). In the beginning of XX century term tortuosity was adopted in medicine to describe (qualitatively) spatial curvature of blood vessels (see, for example Edington (1901) or Cairney (1924). Later, Carman (1939) suggested to use this term to describe curvilinear character of porous space in the context of hydraulic conductivity. Carman defined it as the ratio of the effective length (L_e) of the fluid flow path to the apparent length (L_a) of a specimen:

$$\tau_C = L_e / L_a \tag{2.2}$$

(subscript C stays for definition of Carman).

Due to obvious uncertainty of this definition and difficulties associated with its practical implications, Wyllie and Rose (1950), Winsauer et al (1951), and Cornell and Katz (1953) suggested to use different kind of tortuosity τ related to the resistivity factor F (sometimes this factor is also called electrical formation factor or electrical retardation factor):

$$F \equiv k^0 / k^{eff} = \tau / \psi \quad , \tag{2.3}$$

where k^{eff} is the bulk (effective) electrical conductivity of the porous material completely saturated by electrolyte, k^0 is the conductivity of the electrolyte, and ψ is the ratio of the apparent cross-sectional area of the conducting electrolyte to the total cross-sectional area of the specimen. This ratio, however, varies from one cross-section to another and it is unclear, which value is appropriate – maximum, minimum, average or anything else (see Sevostianova et al, 2010).

Perkins et al (1956) suggested an experimental procedure to estimate tortuosity τ and showed that, for completely saturated sandstone, the resistivity factor, tortuosity and porosity p are interrelated by

$$F = \tau^2 / p = k^0 / k^{eff} , \tag{2.4}$$

It means, in particular, that parameter ψ in (2.3), porosity, and tortuosity are interrelated by

$$\psi = p / \tau \tag{2.5}$$

<u>*Remark*</u>. An important consequence of the tortuosity definition according to (2.4) is its tensor character. Indeed, since electrical conductivity is a symmetric second rank tensor, it immediately follows from (2.4) that tortuosity is also a symmetric second rank tensor such that

$$\tau_{ij}\tau_{jk} = k_{ij}^0 \left(k_{jk}^{eff}\right)^{-1} / p \tag{2.6}$$

For isotropic materials $\tau_{ij} = \tau\delta_{ij}$, and the tortuosity can be considered as a scalar.

Note, that definition of tortuosity via electrical conductivity does not clarify the micromechanical meaning of this parameter (it is still unclear, how it can be evaluated from, say, photomicrographs of a porous material), however, it allows one to easily obtain variational bounds for tortuosity using known results for conductivity. Namely, Hashin-Shtrikman bound for conductivity of a porous material is (Hashin and Shtrikman,1962)

$$\frac{2p}{3-p} \geq \frac{k^{eff}}{k^0} = \frac{1}{F} = \frac{p}{\tau^2} . \tag{2.7}$$

It immediately yields the corresponding bound for tortuosity:

$$\tau^2 \geq 1 + \frac{1-p}{2} \tag{2.8}$$

Similarly, Beran's bound for conductivity has the following form (Beran 1965, 1968)

$$\frac{2\zeta\, p}{1+2\zeta - p} \geq \frac{k^{eff}}{k^0} = \frac{1}{F} \tag{2.9}$$

This inequality involves the microstructural parameter ζ expressed in terms of three-point correlation function as follows:

$$\zeta = \lim_{\Delta\to 0}\lim_{\Delta'\to\infty}\frac{9}{2p(1-p)}\int_{\Delta}^{\Delta'}\int_{\Delta}^{\Delta'}\int_{-1}^{1}\frac{S_3(r,s,\mu)}{rs}P_2(\mu)d\mu\, dr\, ds \qquad (2.10)$$

where $S_3(r,s,\mu)$ is the three-point spatial correlation function and $P_2(\mu)=(3\mu^2-1)/2$ is Legendre polynomial of order 2. Inequality (2.9) yields the corresponding relation for tortuosity:

$$\tau^2 \geq 1+\frac{1-p}{2\zeta} \qquad (2.11)$$

Definition (2.3) was adopted (with slight modification) by Helmer et al (1995) to describe mass transfer in tumor:

$$\tau_H \equiv D^0 / D^{eff} \qquad (2.12)$$

where D^{eff} is the effective mass transfer coefficient of the material and D^0 is the mass transfer coefficient of the conducting phase (the second phase is assumed to be impenetrable). Namely definition (2.12) is presently used in the biomedical applications for analysis of the properties of tumor. This definition is slightly inconsistent with (2.4) - τ_H in (2.12) is actually a retardation factor rather than tortuosity, as discussed by Clennell (1997).

Pride (1994) has shown that electrical tortuosity (2.3) is one of four fundamental properties of a porous medium that are measurable, and rigorously interrelated (the others are porosity, steady hydrodynamic permeability and the electrical length-scale lambda). This rigorous definition does not involve the concept of an effective path length (2.2). Steady-state tortuosity represents an average of transport through all available flow pathways. The details of pore structure are only resolved if we consider unsteady transport processes.

Application of tortuosity concept to different phenomena has been discussed in detail by Clennell (1997). He pointed out that tortuosity means different things to different people. He distinguished between geometrical tortuosity (objective characteristic of the pore structure). The second class of tortuosity measures are 'retardation factors' extracted from the transport properties of the porous medium. Electrical tortuosity (2.3), and the diffusional tortuosity (2.12) are examples. Third, he considers tortuosity parameters that enter into some simplifications of a real pore space, such as a network model. Finally, he mentioned tortuosity as an adjustable parameter in empirical models. He pointed out that, different tortuosities can be compared if one converts the transport to an overall flux, and compares the efficiency of the transport in the specimen with an idealized case that has maximum efficiency. Due to that, it is possible to prove that the electrical tortuosity (2.3) and diffusional tortuosity (2.12) are identical in the steady state, i.e.

$$F = \tau_H \tag{2.13}$$

In the present work we use this result to establish explicit cross-property connection between the said properties. The existing results has been developed under assumption that one of the phases is electrically insulating (note that the definitions of (2.3) and (2.12) assume that one of the phases is conductive and one is insulating). The concept of the tortuosity is not strictly defined for the systems in which both the phases are electrically conductive and open for diffusion. To extend the concept of tortuosity to this case, we use the replacement relations approach recently developed by Chen *et al*. (2017a).

3. Two phase material with conductive constituents: replacement relations for electrical conductivity.

In this section we extend the applicability of the tortuosity parameter to the case, when both the phases are electrically conductive and penetrable for diffusion. For this goal, we consider the problem of the change in overall electric properties of a material upon the changing properties of one of its phases (replacement relations) (see Figure 1). For elastic properties, this problem was first addressed by Gassmann (1951) who derived relation expressing bulk and shear moduli of fully saturated rock in terms of the elastic properties of dry rock. Further development of Gassmann's equation was done in the works of Han and Batzle (2004) and Ciz and Shapiro (2007). Sevostianov and Kachanov (2007), formulated the replacement relations in terms of property contribution tensors. Their results are valid for anisotropic materials (including anisotropic constituents) and can be rewritten for other physical properties as well. For the thermal conductivity problem, replacement relations have been first formulated by Zimmerman (1989) for isotropic air and water saturated rock. It was generalized to the case of anisotropic two-phase material by Chen et al (2017 a) as:

$$\boldsymbol{r}_{eff} = \boldsymbol{r}_0 + \phi\left[\left(\boldsymbol{r}_1 - \boldsymbol{r}_0\right)^{-1} + \phi\left(\boldsymbol{r}_{ins} - \boldsymbol{r}_0\right)^{-1}\right]^{-1} \tag{3.1}$$

where ϕ is the volume fraction of phase "1", $\boldsymbol{r}_0$ and $\boldsymbol{r}_1$ are electrical resistivities of two phases, $\boldsymbol{r}_{eff}$ is overall resistivity of the composite, and $\boldsymbol{r}_{ins}$ is the resistivity of the comparison two phase material that has the same morphology and $\boldsymbol{r}_0$, but $\boldsymbol{r}_1 \to \infty$. The replacement relation (3.1) has the same form for any homogenization method (assuming that the properties of materials with insulating and conducting inhomogeneities are calculated with the same method, of course).

In the case of the isotropic mixture of two isotropic phases, expression (3.1) can be rewritten in the form:

$$\phi \frac{k_{eff}}{k_0 - k_{eff}} - \phi \frac{k_{ins}}{k_0 - k_{ins}} = \frac{k_1}{k_0 - k_1} \tag{3.2}$$

where k_{eff} is overall conductivity of the composite with both phases being conductive and having conductivities k_0 and k_1 (Fig 2a), and k_{ins} is the overall conductivity of the comparison composite having the same morphology with one phase of conductivity k_0 and another phase being a perfect insulator.

Similar replacement relation can be derived for the mass transfer (diffusion) coefficient as well. Indeed, following Knyazeva *et al* (2015), let us consider a reference volume V of a material with the isotropic diffusion coefficient D_0 containing inhomogeneity with diffusion coefficient D_1 occupying domain $V_1 << V$. We assume that both inhomogeneity and the surrounding material satisfies the linear Fick's law connecting concentration gradient with the mass transfer rate (molar flux). The homogeneous boundary conditions (Hill, 1963) are assumed: the "remotely applied" concentration gradient, or molar flux, is uniform in the absence of the inhomogeneity. Let, for example the molar flux $\boldsymbol{J}_0$ be prescribed at the boundary of V. Then, the average over $V = V_0 \cup V_1$ concentration gradient ∇c of the diffusant is related to $\boldsymbol{J}_0$ by

$$\langle \nabla c \rangle_V = \left[D_0 \boldsymbol{I} + \frac{V_1}{V} \boldsymbol{H}^{DR} \right] \cdot \boldsymbol{J}_0. \tag{3.3}$$

where tensor $\boldsymbol{H}^{DR}$ can be called the diffusion resistance contribution tensor. For a spheroidal inhomogeneity, in the absence of segregation at the interface,

$$\boldsymbol{H}^{DR} = \frac{1}{D_0} \left[\frac{(D_0 - D_1)}{D_0 + (D_1 - D_0) f_0} (\boldsymbol{I} - \boldsymbol{nn}) + \frac{(D_0 - D_1)}{D_1 - 2(D_1 - D_0) f_0} \boldsymbol{nn} \right] \tag{3.4}$$

shape factor f_0 is expressed in terms of the spheroid aspect ratio γ as follows

$$f_0 = \frac{\gamma^2(1-g)}{2(\gamma^2-1)} \tag{3.5}$$

with

$$g(\gamma) = \begin{cases} \dfrac{1}{\gamma\sqrt{1-\gamma^2}} \arctan\dfrac{\sqrt{1-\gamma^2}}{\gamma}, & \text{oblate shape } (\gamma < 1) \\ \dfrac{1}{2\gamma\sqrt{\gamma^2-1}} \ln\dfrac{\gamma+\sqrt{\gamma^2-1}}{\gamma-\sqrt{\gamma^2-1}}, & \text{prolate shape } (\gamma > 1) \end{cases} \tag{3.6}$$

We can rewrite expression (3.4) as

$$\left(\boldsymbol{H}_1^{DR}\right)^{-1} = \frac{D_1 D_0}{D_1 - D_0}\boldsymbol{I} + D_0\left[(f_0-1)(\boldsymbol{I}-\boldsymbol{nn}) - 2f_0\boldsymbol{nn}\right] \tag{3.7}$$

If phase 1 is impenetrable for a diffusant ($D_1 \to 0$),

$$\left(\boldsymbol{H}_{imp}^{DR}\right)^{-1} = D_0\left[(f_0-1)(\boldsymbol{I}-\boldsymbol{nn}) - 2f_0\boldsymbol{nn}\right] \tag{3.8}$$

Subtracting (3.8) from (3.7)

$$\left(\boldsymbol{H}_1^{DR}\right)^{-1} - \left(\boldsymbol{H}_{imp}^{DR}\right)^{-1} = \frac{D_A D_0}{D_A - D_0} = \left(\frac{1}{D_A} - \frac{1}{D_0}\right)^{-1} \tag{3.9}$$

In the case of the isotropic mixture of two isotropic phases, expression (3.9) yields the following replacement relation for diffusion coefficients (that has the same form as (3.2)):

$$\phi\frac{D_{eff}}{D_0 - D_{eff}} - \phi\frac{D_{imp}}{D_0 - D_{imp}} = \frac{D_1}{D_0 - D_1} \tag{3.10}$$

where D_{eff} is effective mass transfer coefficient of the composite with both phases being penetrable for diffusant and having coefficients D_0 and D_1 (Fig 1a), and D_{imp} is the effective diffusion coefficient of the composite having the same microstructure and D_0, while the second phase is impenetrable for the diffusant (Fig 2b). Expression (3.10) completely coincides with (3.2). As discussed by Chen et al (2017 b), replacement relation have the same shape in all the homogenization schemes based on the concept of effective field – Mori-Tanaka-Benveniste, Kanaun-Levin, Maxwell, etc.

Note, that the replacement relations (3.2) and (3.10) are approximate - they turn to be exact only in the case when one of the phases is represented by isolated ellipsoidal inhomogeneities. This approximation, however, shows good accuracy for rather irregular microstructures, as shown by application of its more complex elastic analogy - Gassmann's equation - in geophysics (Berryman, 1999; Avseth et al, 2006).

4. Connection between electric conductivity and diffusion coefficient.

In this Section we derive the connection between electric conductivity and diffusion coefficient of an isotropic two-phase material when both phases are electrically conductive and penetrable for a diffusant (to evaluate the overall diffusion coefficient from the electric conductivity measurements). For this goal we express both properties using replacement relations (3.2) and (3.10) and tortuosity parameter that is common for both the properties.

We start with equations (2.3) and (2.4) that express retardation factor for conductivity as $F \equiv k^0 / k^{eff}$. Substitution of this expression into (3.2) yields

$$\frac{k_{eff}}{k_0 - k_{eff}} - \frac{1}{F-1} = \frac{1}{\phi}\frac{k_1}{k_0 - k_1} \tag{4.1}$$

Thus the resistivity factor (retardation factor for conductivity) F is expressed in terms of effective conductivity of the composite k_{eff} and conductivities of its two phases, k_0 and k_1 as

$$F = 1 + \frac{\phi(k_0 - k_1)(k_0 - k_{eff})}{\phi k_{eff}(k_0 - k_1) - k_1(k_0 - k_{eff})} \tag{4.2}$$

In the same manner, combining (3.10) with (2.12), we can write for the effective mass transfer coefficient

$$\frac{D_{eff}}{D_0 - D_{eff}} - \frac{1}{\tau_H - 1} = \frac{1}{\phi}\frac{D_1}{D_0 - D_1} \tag{4.3}$$

Taking into account (2.13), we can obtain, after some algebra, from (4.2) and (4.3)

$$D_{eff} = D_0 \frac{BD_A + \phi(D_0 - D_1)}{\phi(B+1)(D_0 - D_1) + BD_1} \tag{4.4}$$

where

$$B = F - 1 = \frac{\phi(k_0 - k_1)(k_0 - k_{eff})}{\phi k_{eff}(k_0 - k_1) - k_1(k_0 - k_{eff})} \qquad (4.5)$$

Figure 2 illustrates behavior of function B for different values of k_{eff} and k_1.

Expressions (4.4) and (4.5) constitute the cross-property connection between overall diffusion coefficient and electrical conductivity of a two phase isotropic material where both the phases are electrically conductive and penetrable for a diffusant. Since this cross-property connection is based on approximate replacement relations (3.2) and (3.10), their accuracy must be verified. In the next section we do it using finite elements method.

5. Computer simulation.

To verify expression (4.4), we model the material microstructure using interpenetrating spheres that are randomly located in a reference volume. We start with sphere packing in a unit cell (UC) following procedure described by Drach et al (2016). The main challenge is the surface re-meshing required to remove overlapping regions and achieve a consistent error-free surface mesh suitable for 3D meshing. It has been done using voxelization method described by Nooruddin and Turk (2003). The idea of the method is to create a regular array (corresponding to a 2D projection of the model) of parallel (voxel-size spaced) rays going through the 3D model and determine the intersection between rays and model polygons. The voxel representation of the model is then constructed based on the determined intersections. Once the voxelization is completed we can reconstruct the surface mesh. For this goal, we used Marching Cubes algorithm (Lorensen and Cline, 1987) implemented in Matlab function called "isosurface.m" that extracts a polygonal mesh of an isosurface from voxels (cuberille grid). In order to generate equal element size structure and produce smoothed model we utilize smoothing method (Taubin, 1995). The final structure is presented in the Figure 3a. The surface mesh was imported into commercial FEA software MSC Marc/Mentat for preparation of the model and subsequent analysis. The UC is auto meshed with non-linear tetrahedral 3D elements (see Figure 3b). In FEM analysis, we considered microstructures with volume fractions of phases varying from 30% to 70%.

After generating the volume mesh material properties have been assigned to the phases. We used the ratio $k_0/k_1 = 1.5$ and varied D_1/D_0 from 2 to 10. Two types of boundary conditions are considered to find non-zero components of the tensors of effective properties D_{eff} and k_{eff}:

uniform gradients of diffusant concentration and electric potential on the faces of the reference volume, respectively. The non-zero components of the effective mass transfer tensors are found from the set of three loading cases: concentration gradient along global coordinate axes x_1, x_2, and x_3. In the similar way effective conductivity tensors are found from the set of the following cases: electric potential gradient along x_1, x_2, and x_3 coordinate axes. Once the boundary conditions are prescribed, FEM simulations are performed, and the result files are processed using a custom Python script to determine D_{eff} and k_{eff} tensors utilizing Fick's and Ohm's laws respectively and to analyze the possibility of cross-property connection between effective electric conductivity and mass transfer coefficient of a two phase material. Figure 3 illustrates comparison of effective diffusion coefficient obtained from FEA calculations and from cross-property connection (4.4) using FEA calculations for electrical conductivity. For reader's convenience, we also give the results in the form of Table in the Appendix. It is seen that the even at $D_1/D_0 = 5$ (while $k_0/k_1 = 1.5$) the accuracy of the cross-property connection is better than 8% for the entire range of ϕ.

6. Discussion and conclusion.

We developed a cross-property connection between effective electric conductivity and diffusion coefficient of a two phase material with both phases being electrically conductive and penetrable for the mass transfer. The results are aligned with the general cross-property connections approach originally developed by Sevostianov and Kachanov, 2002 (see their review of 2009). It is based on the quantitative analysis of the microstructural factors governing different physical properties of materials. Electrical and mass transport properties of a material with interpenetrating phases are governed by phase tortuosities - parameter that was originally developed for the cases when only one of the phases is electrically conductive. We used the replacement relations for conductivity and mass transfer and extended the tortuosity concept for the case when both phases are conductive and penetrable.

This work was inspired by needs in biomedical engineering related to quantification in the areas of cancer diagnostics and therapy. There is a number of qualitative and phenomenological results in this area – variation of dielectric properties due to cancer has been reported by Peyman et al (2015), correlation between conductivity and prognosis factor in invasive breast cancer has been observed by Kim et al (2016), methods of image analysis for estimation of tortuosity parameters has been used by Baish et al (1996), Bullitt et al (2003, 2005, 2006). Most of the results, however, have descriptive rather than predictive power. The obtained cross-property connection challenges the existing paradigm and aim at changing the situation.

Another important implication of the obtained result is in the monitoring of the tumor therapy process. As pointed out by Bullit et al (2006), "effective monitoring of tumor therapy poses a major clinical problem. If a tumor previously sensitive to a drug later becomes resistant, the therapeutic regimen should be changed rapidly. Unfortunately, there is presently no reliable, noninvasive means of monitoring therapeutic efficacy". Quantitative description of the improvement of vessel tortuosity abnormalities during the therapy is still the open question - the existing methods of the evaluation of tortuosity from photomicrographs or ultrasound, acoustic, or MRI images (Sevostianova et al 2010, Shelton et al, 2015; Rao et al, 2016) do not provide sufficient accuracy. Results obtained in the present paper allows one to solve this problem if the tortuosity is understood according to (2.12).

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Figure captions

Figure 1. Sketch of the two materials of the same morphology having insulating (a) and conductive (b) skeletons and filled with the same electrolyte.

Figure 2. Dependence of factor B entering cross-property connection (4.4) on the volume fraction of phase for different values of k_{eff} and k_1.

Figure 3. Example of a two phase material with equal volume fraction : a) geometry; b) 3D meshed structure.

Figure 4. Effective mass transfer coefficients obtained by direct FEA calculations (symbols) and calculated from effective electric conductivities using cross-property connection (4.4) (lines). $k_1/k_0 = 2/3$. Solid line and diamonds: $D_1/D_0 = 2$; dashed line and circles $D_1/D_0 = 5$; dot-dashed line and triangles: $D_1/D_0 = 10$.

Appendix.

Table A1. Comparison of D_{eff}/D_0 calculated directly by FEM (**Direct**) with ones obtained using cross-property connection (4.4) and calculated data for k_{eff} (**(4.4)**). Error is given in %. $k_1/k_0 = 2/3$

ϕ	$D_1/D_0 = 2$			$D_1/D_0 = 5$			$D_1/D_0 = 10$		
	Direct	**(4.4)**	**Error**	**Direct**	**(4.4)**	**Error**	**Direct**	**(4.4)**	**Error**
0.290	1.243	1.232	0.875	1.737	1.765	-1.621	2.296	2.499	-8.843
0.294	1.247	1.235	0.946	1.758	1.772	-0.758	2.315	2.498	-7.911
0.294	1.248	1.236	0.946	1.760	1.773	-0.758	2.324	2.501	-7.637
0.346	1.293	1.281	0.916	1.899	1.911	-0.611	2.420	2.708	-11.890
0.350	1.298	1.285	1.038	1.930	1.918	0.629	2.558	2.704	-5.735
0.355	1.303	1.289	1.069	1.946	1.927	0.946	2.655	2.714	-2.226
0.389	1.335	1.319	1.220	2.079	2.018	2.897	2.844	2.853	-0.313
0.396	1.341	1.326	1.154	2.085	2.043	2.044	3.031	2.901	4.302
0.416	1.361	1.344	1.250	2.172	2.099	3.372	3.157	2.991	5.264
0.434	1.378	1.360	1.284	2.239	2.153	3.835	3.135	3.082	1.678
0.461	1.404	1.385	1.374	2.345	2.235	4.687	3.579	3.229	9.787
0.463	1.407	1.387	1.428	2.362	2.239	5.212	3.658	3.228	11.757
0.498	1.441	1.421	1.378	2.487	2.363	4.986	3.777	3.466	8.226
0.501	1.445	1.423	1.496	2.517	2.366	6.011	3.813	3.485	8.614
0.506	1.450	1.428	1.537	2.533	2.379	6.098	3.973	3.470	12.666
0.537	1.483	1.458	1.668	2.684	2.485	7.382	4.408	3.787	14.080
0.541	1.484	1.462	1.521	2.695	2.491	7.574	4.418	3.745	15.244
0.566	1.513	1.486	1.777	2.822	2.586	8.348	4.622	3.882	16.007
0.584	1.532	1.505	1.772	2.902	2.661	8.292	4.990	4.243	14.972
0.604	1.553	1.525	1.800	2.991	2.741	8.354	5.064	4.320	14.701
0.611	1.560	1.533	1.733	3.014	2.776	7.904	5.127	4.592	10.431
0.645	1.596	1.568	1.758	3.171	2.919	7.942	5.467	4.609	15.691
0.650	1.601	1.573	1.768	3.197	2.941	8.001	5.507	4.799	12.865
0.654	1.607	1.577	1.862	3.237	2.955	8.710	5.672	4.884	13.891
0.706	1.662	1.635	1.617	3.455	3.225	6.652	6.246	5.364	14.134
0.706	1.662	1.635	1.617	3.455	3.225	6.652	6.256	5.394	13.779
0.710	1.666	1.639	1.664	3.485	3.240	7.031	6.267	5.378	14.181

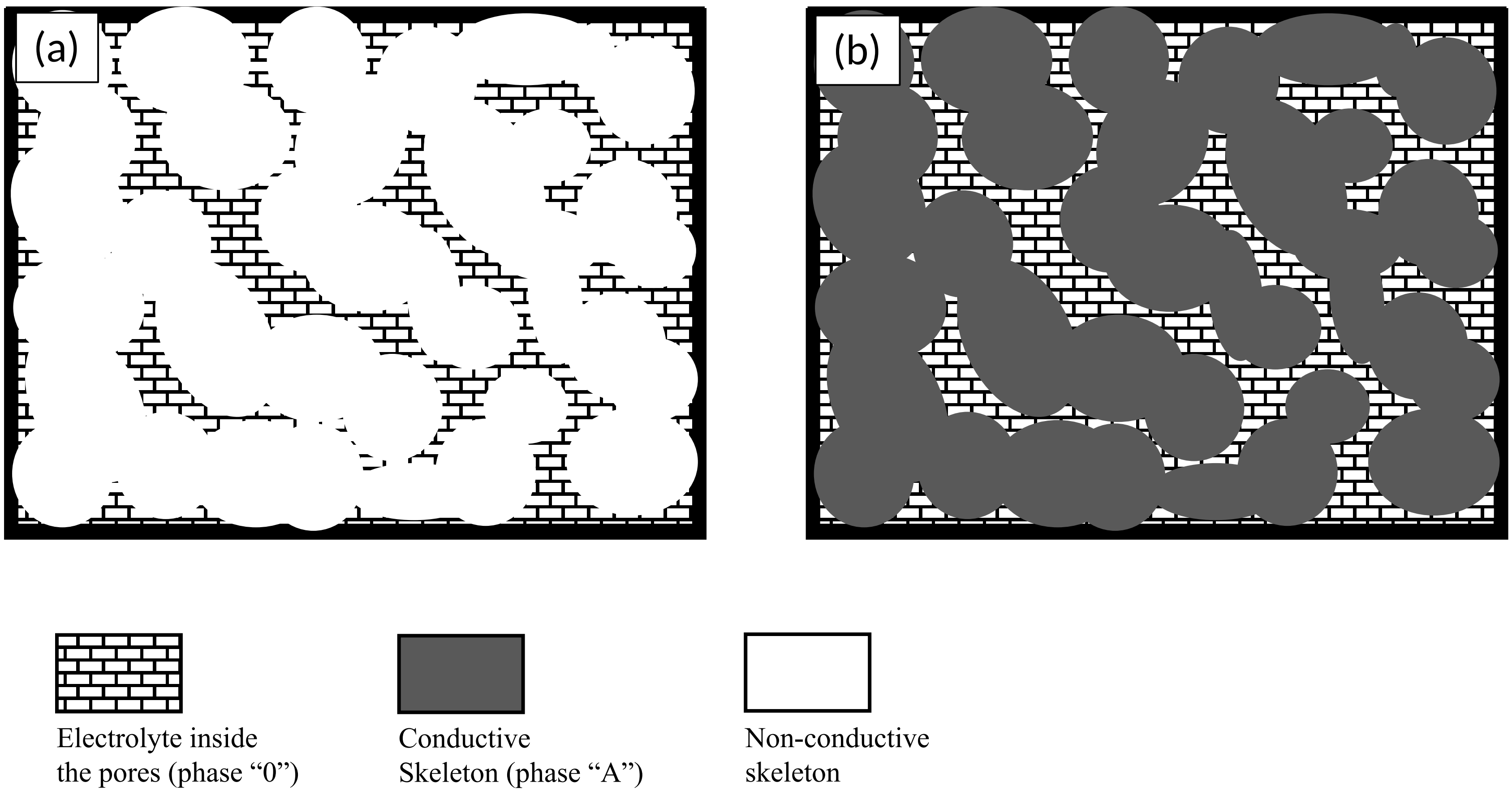
(a)
(b)
Electrolyte inside
the pores (phase “0”)
Conductive
Skeleton (phase “A”)
Non-conductive
skeleton

Figure 1

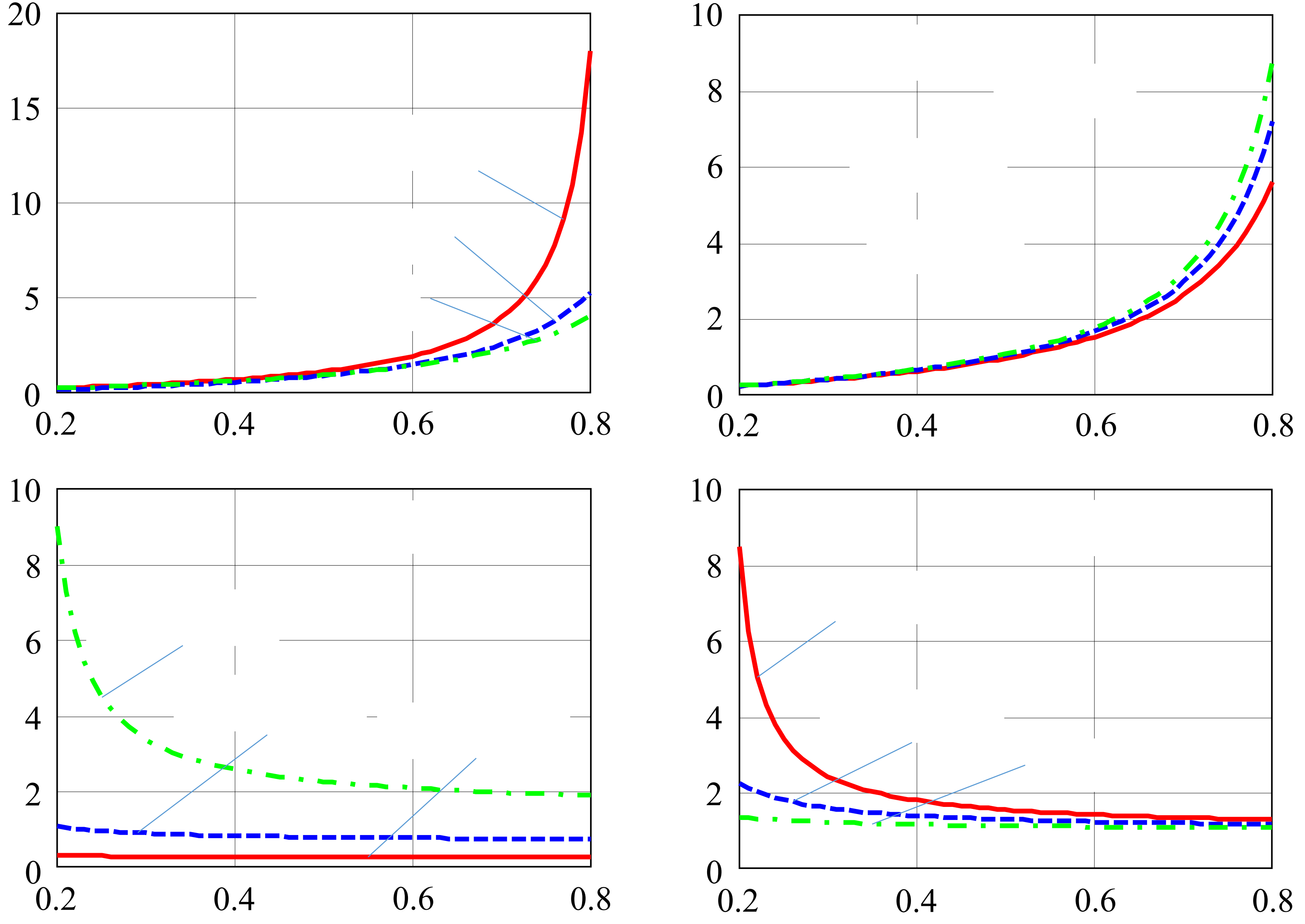

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Figure 2

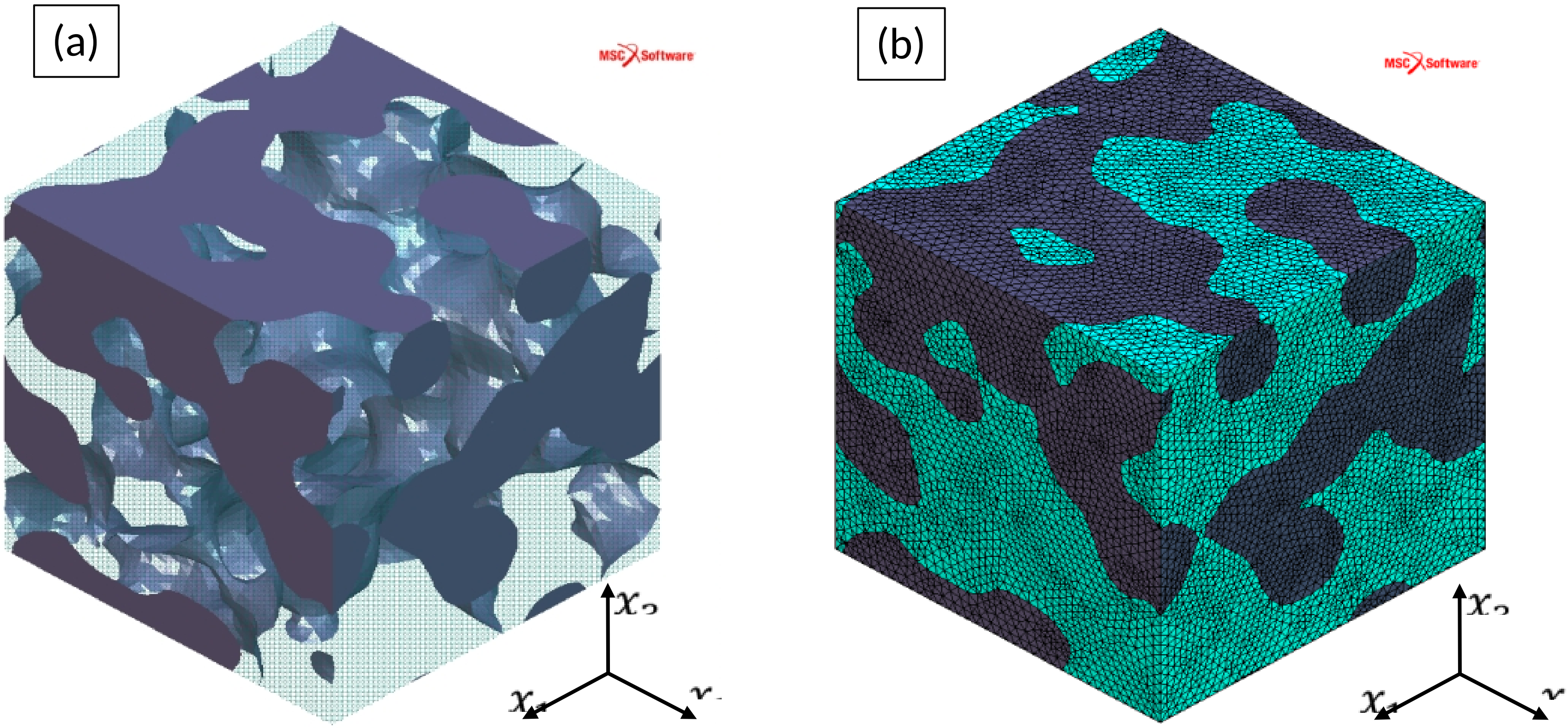

Figure 3

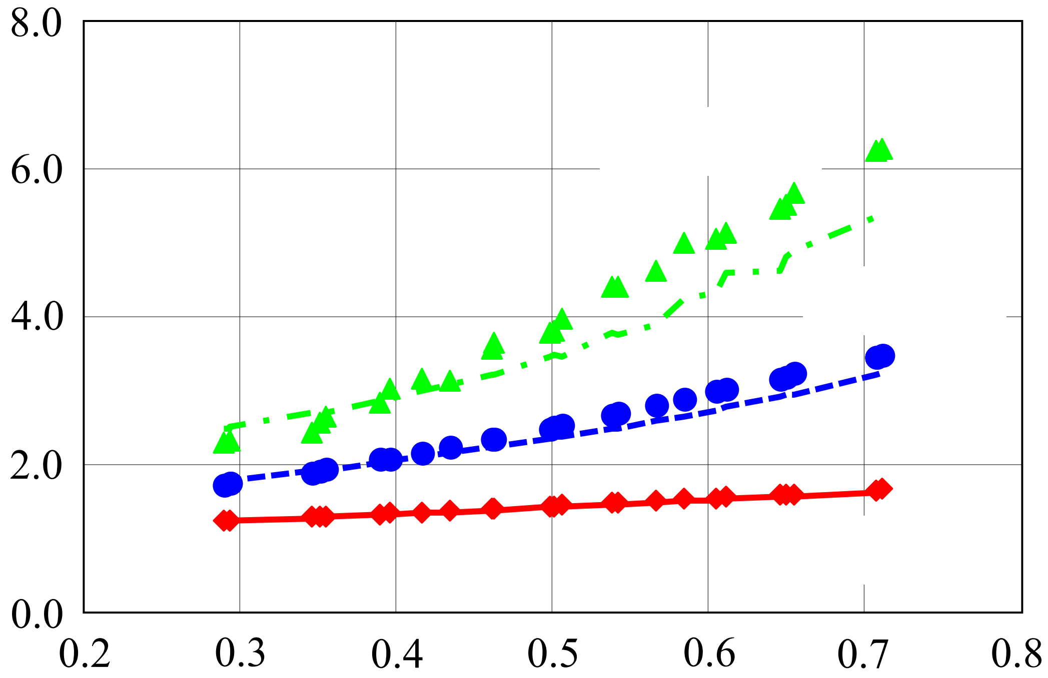

Figure 4