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Some aspects of numerical analysis of conductivity percolation threshold

Milan Ambrožič *, Aleš Dakskobler
Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

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Abstract

We consider theoretically some geometrical aspects of the conductivity-percolation problem, where the spherical conducting particles are embedded in an insulating ceramic matrix. We consider four aspects: the probability of the inter-penetration of conducting particles for different penetration depths, inhomogeneous spatial distribution of particles in the insulating matrix, the agglomeration of particles and the presence of pores.

Keywords: Composites; Electrical conductivity; Percolation threshold

1. Introduction

When electrically conducting particles are randomly distributed within an insulating matrix, like in metal–ceramic matrix composites, the whole material may be insulating or conducting, depending on the volume fraction of conducting phase. Just near the percolation threshold, where the critical amount of conducting particles for the onset of electrical conduction is reached, the electrical properties of the material exhibit a non-linear critical behavior.[1–6] Conducting particles of different shapes in two and three dimensions (2D and 3D) are considered in reported calculations of the percolation threshold: mostly spherical,[7–9] thin and thick elongated particles,[10–17] and even 2D random polygons with random plane-orientations in 3D space.[18] With the aim of special algorithms the volume ratios of the conducting component at the percolation threshold for spherical particles in 2D and 3D were calculated even to six digits exactly.[8,9]

In our previous work, we investigated numerically the percolation-threshold-volume fraction of the conducting phase composed of spherical, elongated and brick-like particles in 3D.[19,20] Quantitative analysis of the influence of the shape and other parameters on the threshold-volume fraction was performed. Our results for spherical and elongated particles agree with the results in literature,[9,15,16] while to our knowledge, we were the first to consider brick-like particles with spherically rounded edges. In this paper, we limit our calculations to spherical particles (spheres), and we consider some additional geometrical aspects.

2. Model

We take a rectangular cell with dimensions $L_x \times L_y \times L_z$, typically $1 \times 1 \times 1$ and take as the electrodes the plates at $z = 0$ and $z = L_z$, as shown in Fig. 1. We measure all lengths, e.g., the diameter d of the spherical particles, in the scale of cell dimensions.

The procedure for obtaining the volume fraction of conducting phase at the percolation threshold (we call it "percolation-threshold volume" and denote it by v_p) is the following. We sequentially and randomly locate the spheres into the cell and immediately check for the conducting threshold, i.e., whether or not the conductive path has been made by connecting spheres from one electrode to another. At the threshold, we sum the volumes of all the spheres and calculate the percolation-threshold volume. For the same set of parameters, we repeat this procedure several (N_{rep}) times to estimate the average value of the percolation-threshold volume v_p and its statistical deviation from the average δv_p.

We allow spheres to penetrate each other to some extent ("soft-core" particles). The penetration depth is defined as $d_{pen} = R_1 + R_2 - d_C$, where R_1 and R_2 are the radii of a pair of intersecting spheres and d_C is the distance between their centers (Fig. 1). Then we can define a relative penetration depth, RPD, with respect to the radii of both spheres: $\mathrm{RPD} = d_{pen}/R_{min}$, where R_{min} is the smaller radius (if the sizes of the spheres are not homogeneous). The extent of the possible penetration is given by the maximal relative penetration depth, MRPD, which is prescribed for all particles, so that RPD < MRPD must hold for each

* Corresponding author. Tel.: +386 1 477 39 40; fax: +386 1 251 93 85.
E-mail address: milan.ambrozic@ijs.si (M. Ambrožič).

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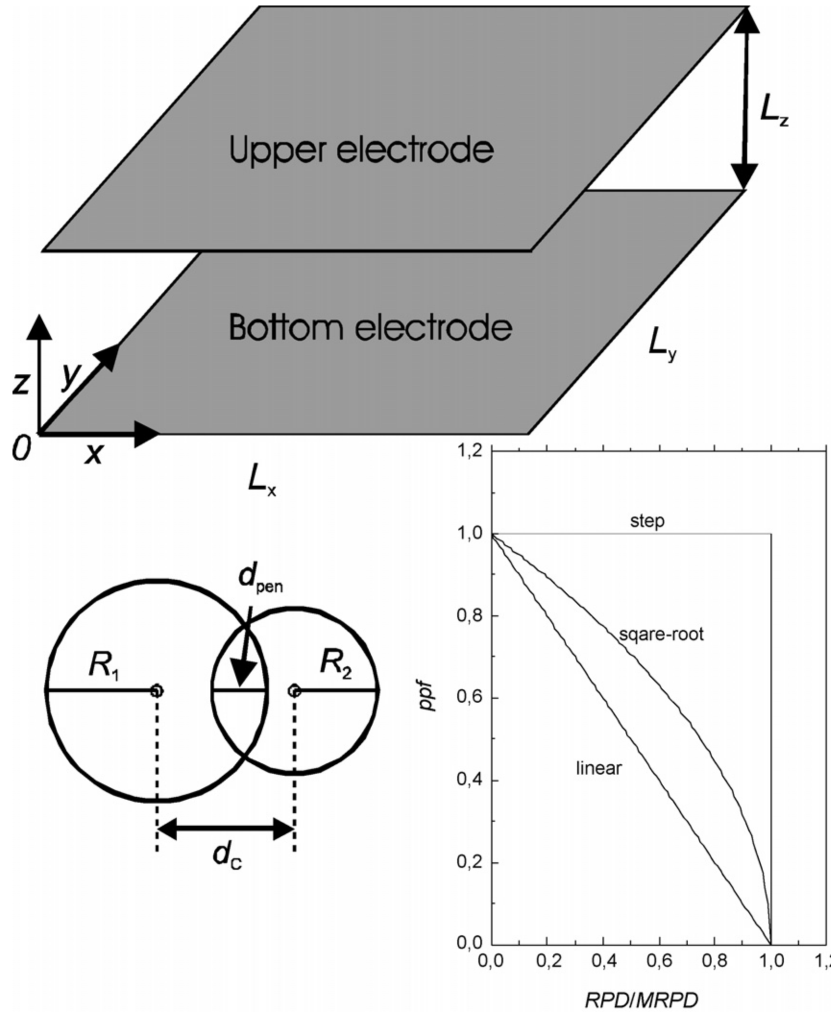

Fig. 1. Coordinate system of rectangular cell and definition of the penetration depth d_{pen} for two intersecting spheres. Three types of penetration probability function (ppf): step, linear and square-root.

intersecting pair. According to the results in the literature and our previous work, we use the typical MRPD of the order of 10%. More details about the model are given in ref.[19]

3. Results and discussion

The percolation-threshold volume, v_p, is strongly influenced by the allowed maximal relative penetration depth, MRPD, which can vary from 0 and 2. In the usually performed model with the prescribed MRPD, we have a simple criterion: a new particle in the cell is automatically accepted if RPD < MRPD with respect to all previously located particles (in the case of penetration). This model corresponds to the step penetration probability function (step ppf) shown in Fig. 1. We can use a penetration probability function (ppf) that diminishes with penetration depth, as shown for linear and square-root ppf in Fig. 1. Then for RPD < MRPD there is a certain probability for the new particle to be accepted; for RPD > MRPD the ppf is zero and the particle is again automatically rejected. We calculated percolation-threshold volumes, v_p, for step, linear and square-root ppf, for different values of MRPD. As expected, v_p is the smallest for step ppf. The results are very sensitive to the MRPD, as well as the type of ppf, therefore we suggest that in the refined percolation models the actual MRPD and ppf should be carefully chosen; alternatively they can be determined to fit the experimental results. In the following calculations we use only the step ppf.

3.1. Spatial non-homogeneity

The non-homogeneity in the distribution of particles' centers in space can have a considerable influence on the percolation-threshold volume and also on the anisotropy of electrical properties of the material. The spatial non-homogeneity can be described by the probability distribution function for the particle-center coordinates, which varies in space. We make simulations with linear probability distribution function for the coordinate x or z, so that we have two possibilities: (a) $w(x) = k_x x + n$ for $0 < x < 1$, while the distribution of y and z coordinates is homogeneous; (b) $w(z) = k_z z + n$ for $0 < z < 1$, while the distri-

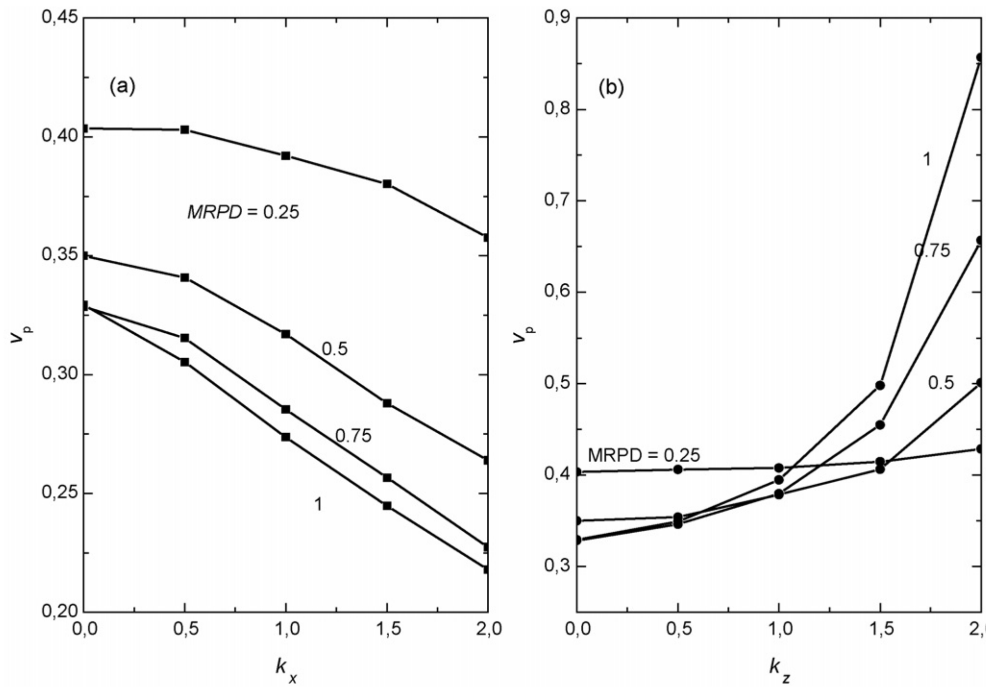

Fig. 2. Percolation-threshold volume dependence on k_x (a) and k_z (b) for different values of MRPD (0.25, 0.5, 0.75 and 1); $d = 0.04$ (equal spheres), $N_{rep} = 30$, δv_p from 2 to 5%.

bution of x and y coordinates is homogeneous. The coefficients k_x and k_z measure the spatial non-homogeneity: the cell is more occupied by spheres at its right or top side, respectively.

Fig. 2 shows the dependence of v_p on the coefficient k_x or k_z for different values of maximal relative penetration depth, MRPD. The percolation-threshold volume decreases with increasing k_x (Fig. 2a), while it increases with increasing k_z (Fig. 2b). Therefore, the percolation threshold can be significantly shifted by the spatial non-homogeneity of the composite.

3.2. Agglomeration of conducting particles

In ref.,[19] we allowed a variation of particles' sizes about the average value of the diameter and found that the larger particle sizes' deviation results in higher percolation-threshold volumes. Here, we analyze the system of two populations of spheres: one with smaller diameter d_{small} and another with much larger diameter d_{big}, typically 5–20 times larger than d_{small}. In the procedure, we first locate a certain number of large spheres, and then continue with locating small spheres until the percolation threshold.

Fig. 3 shows the dependence of the percolation-threshold volume on the relative amount of large spheres. The results strongly depend on the volume ratio of large spheres and to a smaller extent to the difference in the radii of both populations of spheres. The results for the largest spheres, which are 20 times larger than small spheres, are statistically less reliable because the three data points correspond to one to three large spheres in the cell only; nevertheless they follow the same trend as in the case of smaller large spheres.

These results confirm our previous assertion that the greater diversity of particles' dimensions results in larger percolation-

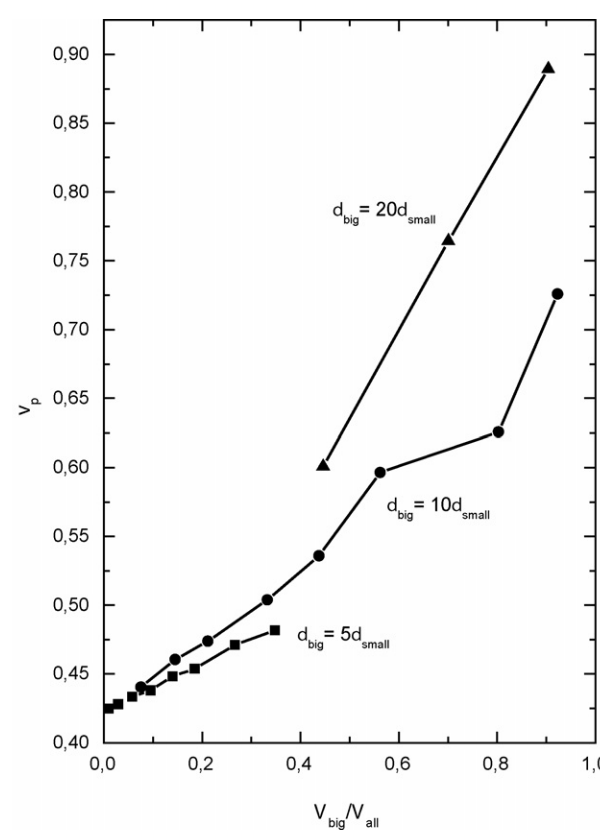

Fig. 3. Percolation-threshold volume dependence on the volume ratio of larger particles (agglomerates) within the volume of conducting phase. Diameter of small spheres is $d_{small} = 0.04$, while the diameter of large spheres is $d_{big} = 5$, 10 or 20 d_{small}; MRPD = 0.2; $N_{rep} = 40$; δv_p is 2% or more. V_{big} and V_{all} denote the sum of the volumes of large spheres, and all the spheres, respecively.

threshold volume. The large spheres in our model could represent agglomerates of conducting particles in the real composite system.

3.3. The effect of pores

A similar procedure as for inserting the large (agglomerated) particles into the cell as described in previous section can be used to study the influence of large pores in the matrix. Pores can be treated as insulating spheres in the cell, which are located prior to inserting conducting particles. It is expected that the pores increase the percolation-threshold volume of conducting particles, which is calculated with respect to the volume of the cell from which the volume of pores is subtracted. Calculations show that the porosity should be greater than 20% in order to increase v_p significantly.

4. Conclusion

We investigated numerically some geometrical aspects of the electrical conductivity percolation threshold for spherical conducting particles in an insulating matrix. The percolation-threshold volume depends significantly on the maximal relative penetration depth and the penetration probability function of soft-core particles, non-homogeneity and agglomeration of the particles, and also on the porosity of the material.

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