EFFECTIVE THERMAL CONDUCTIVITY OF PARTICULATE COMPOSITE MATERIALS

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On the basis of a mean field approximation method (MFAM) the formula for effective thermal conductivity of particulate composite was derived. In the case of binary system, it was shown that there exists the percolation phase transition. The MFAM gives only classical critical index t near to the percolation phase transition (critical region). That is the reason for a generalization of the formula for effective thermal conductivity by introducing parameter t dependent on the volume fraction and in the critical region complying with the results obtained by lattice Monte Carlo simulations.

Key words: thermal conductivity, effective thermal conductivity, volume fraction, percolation threshold, percolation phase transition

EFEKTÍVNA TEPELNÁ VODIVOSŤ ČASTICOVÝCH KOMPOZITNÝCH MATERIÁLOV

Na základe metódy stredného poľa bola odvodená formula pre efektívnu tepelnú vodivosť časticového kompozitu. Existencia perkolačného fázového prechodu bola preukázaná pri binárnom systéme. Metóda stredného poľa poskytuje iba klasický kritický index t v blízkosti perkolačného fázového prechodu (kritická oblasť). Toto bol dôvod na zovšeobecnenie formuly pre efektívnu tepelnú vodivosť tak, aby v kritickej oblasti parameter t zodpovedal výsledkom získaným simuláciami Monte Carlo na mriežke.

1. Introduction

The aim of this paper is to derive the relation for effective thermal conductivity of particulate composite materials whose granules are coated by some other material. The particulate composite consists of granules, possibly in a matrix. These materials have an application in industry. For example, the mixture copper-graphite particulate composite material [1] is used for electrical contacts carrying current between stationary and rotating parts of electromotors, generators, seam welding machines, etc. Special properties of these contacts are required, especially for the

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electrical and thermal conductivity. It was shown that such requirements are satisfied best by a composite material composed of matrix showing high electrical conductivity while graphite in the form of globular granules creates the secondary phase in the copper matrix ensuring high sliding properties. For improvement of adhesion between matrix and the graphite granules, the latters are to be coated by a suitable material [2] and [3].

For application of these composites it is important to know their mechanical (effective Young's modulus [4]), thermomechanical (thermal expansion) and thermophysical (effective thermal conductivity) properties. Before we start to derive the relation for effective thermal conductivity, we introduce some general remarks about the composite materials. Generally, the composite material is heterogenous at the submacroscopic level (for the length scale of linear dimension of granules) as it is composed of components, which, on the one hand, are spatially separated from each other (insoluble components) and, on the other hand, are randomly distributed over the whole sample. Due to this randomness the physical quantities of the composite on the submacroscopic level are not only dependent on space coordinates but they are also random quantities. The processes at the submacroscopic level are described by phenomenological stochastic equations. The use of the phenomenological equations requires fulfilling certain conditions. However at the macroscopic level the composite is usually homogeneous and sometimes even isotropic and may be characterized by effective parameters independent of space coordinates. Necessary and sufficient conditions for using effective parameters are discussed in Beran's work [5]. In the further text we assume that all conditions for using the effective parameters are satisfied.

For an experimentalist it is very important to know in which cases the composite material at the macroscopic level may be characterized by effective parameters because only in these cases it is justifiable to use the standard methods for their measurement. If one uses phenomenological equations for derivation of the relations for effective parameters, then the linear dimensions of granules have to be much larger than the mean free path of carriers which participate on the transport of mass, energy and charge. But, on the other hand, they have to be much smaller with respect to macroscopic linear dimensions of inhomogeneities.

In the process of derivation of the relations for effective parameters, we encounter the question how the effective parameters depend on the structure of composite at the submacroscopic level and on the properties of individual components of composite material, as well. This information is very important, especially for a technologist. Knowing the relations for effective parameters, it is possible to produce composite material with the prescribed values of the parameters (materials "tayloring"). The statistics of the structure of composite at submacroscopic level is very often unknown, and only the volume fractions are known from the manufacturing process.

The derivation of the relation for effective thermal conductivity is a very difficult problem. When solving this problem, one has to deal with two difficulties. The first one is connected with the necessity to know the statistics of the structure of the composite at submacroscopic level, which is usually unknown. The second one is connected with the mathematical difficulties of exact calculation of effective thermal conductivity, and, therefore, one is obliged to use approximate methods. One of those approximate methods is the mean field approximation method (MFAM), which is used in this paper.

2. Mean field approximation

The mean field approximation method is based on the idea that a randomly chosen isotropic granule characterized by the thermal conductivity λ_n is submerged into an unlimited effective medium, which is characterized by the effective thermal conductivity λ_{eff}. The MFAM assumes that the properties of an effective medium are not changed by putting the granule in it. The thermal conductivity, as it was mentioned before, is a stochastic quantity, which is determined by n-point correlation functions. The MFAM does not require knowledge of the n-point correlation functions, but only the local distribution function, which is determined by the volume fractions. This fact may be advantageous, but, due to this fact, the method is only approximate because it uses incomplete information about the statistics of the structure of the composite at the submacroscopic level. It can be shown that in the case of a weak inhomogeneity the MFAM may give results of sufficient accuracy. The derivation of the relations for effective thermal conductivity is based on usage of the stationary heat equation. In the following paper the derivation of the relations for effective parameters will be based on the non-stationary heat equation.

3. Effective thermal conductivity of the particulate composite material

We consider granules of globular form whose diameter is sufficiently large (granule consists of many particles) so we can describe the heat conduction in the granule by the Fourier law

$$\boldsymbol{q} = -\lambda \operatorname{grad} T \tag{1}$$

and by the stationary heat equation

$$\operatorname{div} \boldsymbol{q} = 0, \tag{2}$$

where $\boldsymbol{q}$ is the heat flow density, λ is the thermal conductivity, T is the thermodynamic temperature. From relations (1) and (2) the Laplace equation

$$\Delta T = 0 \tag{3}$$

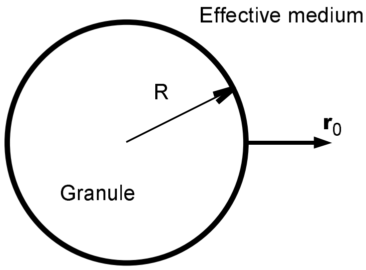

Fig. 1

follows. For the better understanding of the MFAM, we consider the granules at first without the coating, and then we proceed to a more complex case when the granules of certain components are coated. As we mentioned before, the MFAM is based on the idea that the granule is submerged into an unlimited effective medium, therefore we take into account two regions. The first region is the granule of a globular form with radius R, the second one is the effective medium (Fig. 1).

The solution of Eq. (3) in the first and second region reads

$$T_{\mathrm{gr}} = -B\boldsymbol{E}_0 \cdot \boldsymbol{r} \tag{4}$$

and

$$T_{\mathrm{eff}} = -\boldsymbol{E}_0 \cdot \boldsymbol{r} + A\boldsymbol{E}_0 \cdot \frac{\boldsymbol{r}}{r^3}, \tag{5}$$

respectively. The solutions (4) and (5) should satisfy the boundary condition of constant gradient of temperature at the infinity. The constants A and B are determined from the boundary conditions at $r = R$:

$$T_{\mathrm{gr}}(R) = T_{\mathrm{eff}}(R), \tag{6}$$

$$-\lambda \,\mathrm{grad}\, T_{\mathrm{gr}} \cdot \boldsymbol{r}_0 = -\lambda_{\mathrm{eff}} \,\mathrm{grad}\, T_{\mathrm{eff}} \cdot \boldsymbol{r}_0, \tag{7}$$

where $\boldsymbol{r}_0$ is the unit vector perpendicular to the boundary. Relation (7) expresses the equality of the heat flows density. From (4–7) one obtains

$$B = \frac{3\lambda_{\mathrm{eff}}}{2\lambda_{\mathrm{eff}} + \lambda}. \tag{8}$$

Using relations (4) and (8) one can write

$$\mathrm{grad}\, T_{\mathrm{gr}} = -\frac{1}{1 + \dfrac{\lambda - \lambda_{\mathrm{eff}}}{3\lambda_{\mathrm{eff}}}} \boldsymbol{E}_0 \tag{9}$$

and

$$\boldsymbol{q} = -\lambda \,\mathrm{grad}\, T_{\mathrm{gr}} = \frac{\lambda}{1 + \dfrac{\lambda - \lambda_{\mathrm{eff}}}{3\lambda_{\mathrm{eff}}}} \boldsymbol{E}_0. \tag{10}$$

If the composite on the macroscopic level is homogeneous, we can consider:

Assumption I: The probability to find the granule of the n^{th} component in certain place is equal to the volume fraction c_n of the n^{th} component. The probability of finding the granule in a certain place is independent of the probability of finding another granule in another place.

This is truth when the granules are spread out uniformly through the whole sample.

Assumption II: Due to macroscopic character of the instrument for measuring the temperature, the average temperature is measured over a large number of granules of different components. Due to this assumption we can write $\langle T_{\mathrm{gr}}\rangle = T_{\mathrm{exp}}$.

Using Assumptions I and II, we can average relations (9) and (10):

$$\operatorname{grad}\langle T_{\mathrm{gr}}\rangle = -\left\langle \frac{1}{1+\dfrac{\lambda-\lambda_{\mathrm{eff}}}{3\lambda_{\mathrm{eff}}}}\right\rangle \boldsymbol{E}_0 = -\sum_{n=1}^{N} c_n \frac{1}{1+\dfrac{\lambda_n-\lambda_{\mathrm{eff}}}{3\lambda_{\mathrm{eff}}}}\boldsymbol{E}_0, \tag{11}$$

$$\langle \boldsymbol{q}\rangle = \sum_{n=1}^{N} c_n \frac{\lambda_n}{1+\dfrac{\lambda_n-\lambda_{\mathrm{eff}}}{3\lambda_{\mathrm{eff}}}}\boldsymbol{E}_0. \tag{12}$$

$\boldsymbol{E}_0$ is expressed from (11) and substituted into (12):

$$\langle \boldsymbol{q}\rangle = -\frac{\displaystyle\sum_{n=1}^{N} c_n \frac{\lambda_n}{1+\dfrac{\lambda_n-\lambda_{\mathrm{eff}}}{3\lambda_{\mathrm{eff}}}}}{\displaystyle\sum_{n=1}^{N} c_n \frac{1}{1+\dfrac{\lambda_n-\lambda_{\mathrm{eff}}}{3\lambda_{\mathrm{eff}}}}}\operatorname{grad}\langle T_{\mathrm{gr}}\rangle. \tag{13}$$

If the conditions for using the effective thermal conductivity are fulfilled, one can write the Fourier's law in the form

$$\langle \boldsymbol{q}\rangle = -\lambda_{\mathrm{eff}}\operatorname{grad}\langle T_{\mathrm{gr}}\rangle = -\lambda_{\mathrm{eff}}\operatorname{grad} T_{\mathrm{exp}}. \tag{14}$$

Comparing (13) and (14), we obtain

$$\sum_{n=1}^{N} c_n \frac{\lambda_n}{1+\dfrac{\lambda_n-\lambda_{\mathrm{eff}}}{3\lambda_{\mathrm{eff}}}} = \lambda_{\mathrm{eff}}\sum_{n=1}^{N} c_n \frac{1}{1+\dfrac{\lambda_n-\lambda_{\mathrm{eff}}}{3\lambda_{\mathrm{eff}}}}. \tag{15}$$

From (15) it immediately follows that

$$\sum_{n=1}^{N} c_n \frac{\lambda_n - \lambda_{\text{eff}}}{1 + \dfrac{\lambda_n - \lambda_{\text{eff}}}{3\lambda_{\text{eff}}}} = 0. \tag{16}$$

Until now it is not known what is the physical meaning of quantity $\boldsymbol{E}_0$. Eq. (16) yields

$$\sum_{n=1}^{N} c_n \frac{1}{1 + \dfrac{\lambda_n - \lambda_{\text{eff}}}{3\lambda_{\text{eff}}}} = 1, \tag{17}$$

and from it and (11) immediately follows that

$$\boldsymbol{E}_0 = -\operatorname{grad}\langle T_{\text{gr}}\rangle = -\operatorname{grad} T_{\text{exp}}. \tag{18}$$

From Eq. (16), the effective thermal conductivity λ_{eff} can be calculated. The same result was obtained in [6]. The novel contribution of this paper is the derivation of the relation for effective thermal conductivity in the case when the granules of certain component are covered by the surface layer of another material. We will apply the modified method used in [7]. In this case three regions should be considered (Fig. 2). We denote the thermal conductivity of i^{th}-component granule as λ_i and that of the surface layer as $\lambda_{\text{m}i}$. The radius of granule is R_{1i} and together with the surface layer, R_{2i}. The solution of Eq. (3) for individual regions is the following:

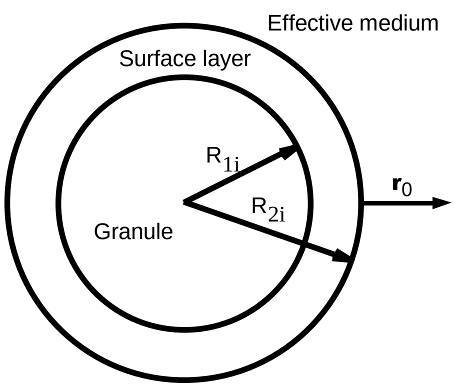

Fig. 2

– in the region of the granule

$$T_i = -B\boldsymbol{E}_0 \cdot \boldsymbol{r} \tag{19}$$

– in the region of the surface layer

$$T_{\text{m}i} = -C\boldsymbol{E}_0 \cdot \boldsymbol{r} + D\boldsymbol{E}_0 \cdot \frac{\boldsymbol{r}}{r^3} \tag{20}$$

– in the region of the effective medium

$$T_{\text{eff}} = -\boldsymbol{E}_0 \cdot \boldsymbol{r} + A\boldsymbol{E}_0 \cdot \frac{\boldsymbol{r}}{r^3}. \tag{21}$$

Constants A, B, C and D are determined from the boundary conditions:
– at $r = R_{1i}$

$$T_i(R_{1i}) = T_{\text{m}i}(R_{1i}), \tag{22}$$

$$-\lambda_i \operatorname{grad} T_i \cdot \boldsymbol{r}_0 = -\lambda_{\text{m}i} \operatorname{grad} T_{\text{m}i} \cdot \boldsymbol{r}_0, \tag{23}$$

– at $r = R_{2i}$

$$T_{\text{m}i}(R_{2i}) = T_{\text{eff}}(R_{2i}), \tag{24}$$

$$-\lambda_{\text{m}i} \operatorname{grad} T_{\text{m}i} \cdot \boldsymbol{r}_0 = -\lambda_{\text{eff}} \operatorname{grad} T_{\text{eff}} \cdot \boldsymbol{r}_0. \tag{25}$$

From (19–25) it follows:

$$C = \frac{1+2\gamma_i}{1-\gamma_i} \cdot \frac{3\lambda_{\text{eff}}}{(2\lambda_{\text{eff}} + \lambda_{\text{m}i})\dfrac{1+2\gamma_i}{1-\gamma_i} + 2\sigma_i(\lambda_{\text{m}i} - \lambda_{\text{eff}})}, \tag{26}$$

$$\frac{D}{R_{1i}^3} = \frac{3\lambda_{\text{eff}}}{(2\lambda_{\text{eff}} + \lambda_{\text{m}i})\dfrac{1+2\gamma_i}{1-\gamma_i} + 2\sigma_i(\lambda_{\text{m}i} - \lambda_{\text{eff}})} \tag{27}$$

where

$$\gamma_i = \frac{\lambda_{\text{m}i}}{\lambda_i}$$

and

$$\sigma_i = \left(\frac{R_{1i}}{R_{2i}}\right)^3.$$

The granule with the surface layer is substituted by the equivalent granule so that the heat flow through the hemisphere of radius R_{2i} must be the same:

$$\begin{aligned} \int\limits_{\Omega(R_{2i})} \boldsymbol{q} \cdot \mathrm{d}\boldsymbol{S} &= \int\limits_{\Omega(R_{2i})} \lambda_{\text{m}i}[C\boldsymbol{E}_0 - \frac{D}{R_{2i}^3}\boldsymbol{E}_0 + 3\frac{D}{R_{2i}^3}\boldsymbol{E}_0 \cdot \boldsymbol{r}_0\boldsymbol{r}_0] \cdot \boldsymbol{r}_0 \mathrm{d}\boldsymbol{S} = \\ &= \int\limits_{\Omega(R_{2i})} \lambda_{\text{m}i}\left[C + 2\frac{D}{R_{2i}^3}\right]\boldsymbol{E}_0 \cdot \mathrm{d}\boldsymbol{S} = \int\limits_{\Omega(R_{2i})} \boldsymbol{q}_{\text{equiv}} \cdot \mathrm{d}\boldsymbol{S}, \end{aligned} \tag{28}$$

where we used (20). From (28) it is obvious that the equivalent heat-flow density is expressed by the relation

$$\boldsymbol{q}_{\text{equiv}} = \lambda_{\text{m}i}\left[C + 2\frac{D}{R_{2i}^3}\right]\boldsymbol{E}_0 = \frac{\lambda_i^*}{1 + \dfrac{\lambda_i^* - \lambda_{\text{eff}}}{3\lambda_{\text{eff}}}}\boldsymbol{E}_0, \tag{29}$$

where the equivalent thermal conductivity, λ_i^*, is expressed by the following relation

$$\lambda_i^* = \lambda_{\text{m}i}\frac{1 + 2\gamma_i + 2\sigma_i(1-\gamma_i)}{1 + 2\gamma_i - \sigma_i(1-\gamma_i)}. \tag{30}$$

Relation (29) was obtained by using (26) and (27). Relation (29) is similar to relation (13) if we use (17). If the first N_1 components consist of coated granules, the effective thermal conductivity can be obtained as a solution of the following equation:

$$\sum_{n=1}^{N_1} c_n \frac{\lambda_n^* - \lambda_{\text{eff}}}{1 + \dfrac{\lambda_n^* - \lambda_{\text{eff}}}{3\lambda_{\text{eff}}}} + \sum_{n=N_1+1}^{N} c_n \frac{\lambda_n - \lambda_{\text{eff}}}{1 + \dfrac{\lambda_n - \lambda_{\text{eff}}}{3\lambda_{\text{eff}}}} = 0. \tag{31}$$

4. Analysis of the obtained results

We shall analyse the case of the binary system. From (31), for the binary system it follows:

$$\lambda_{\text{eff}} = \lambda_1^*\frac{1}{4}\left\{[3c - 1 - (3c-2)r] + \sqrt{[3c - 1 - (3c-2)r]^2 + 8r}\right\}, \tag{32}$$

where c is the volume fraction of the 1^{st} component, $r = \dfrac{\lambda_2}{\lambda_1^*}$. If $\lambda_2 = 0$, the expression (32) transforms to the following form:

$$\lambda_{\text{eff}} = 0; \quad c \leq \frac{1}{3}, \tag{33}$$

and

$$\lambda_{\text{eff}} = \frac{3}{2}\lambda_1^*\left(c - \frac{1}{3}\right); \quad c > \frac{1}{3}. \tag{34}$$

The quantity $c_{\text{k}} = \dfrac{1}{3}$ is called the percolation threshold. For $c < c_{\text{k}}$ the granules of the first component form clusters which are separated from each other and, therefore, a sample is thermally non-conducting ($\lambda_{\mathrm{eff}} = 0$). At $c = c_{\mathrm{k}}$ some clusters connect themselves together and form a percolation cluster, which is spread out through the whole sample. From this moment λ_{eff} is increasing with volume fraction c. The λ_{eff} plays the role of an order parameter. This effect is called percolation and at $c = c_{\mathrm{k}}$ the percolation phase transition takes place. The detailed overview of percolation is given in [8]. In Table 1 the percolation thresholds for different types of lattices are given. These values were obtained by Monte Carlo simulations on different lattices. From the renormalization group analysis, instead of (34), one obtains

$$\lambda_{\mathrm{eff}} = \frac{3}{2}\lambda_1^* \left(c - \frac{1}{3}\right)^t; \quad c > \frac{1}{3}. \tag{35}$$

Table 1

Lattice	c_{k}	t
Honeycomb	0.7	1.15
Square	0.59	1.15
Triangular	0.5	1.15
Simple cubic	0.325	1.725
Body-centered cubic	0.25	1.725
Face-centered cubic	0.195	1.725

It is interesting to note that the parameter t depends only on dimensionality of the sample as it is shown in Table 1. MFAM yields the value $c_{\mathrm{k}} = \dfrac{1}{3}$, which is close to that of the simple cubic lattice.

In the reality, λ_2 is never equal to zero, and, therefore, we cannot observe the percolation phase transition. The smaller is the ratio $r = \dfrac{\lambda_2}{\lambda_1^*}$ the better is the percolation process observable. This fact we shall illustrate in detail, but at first we generalize the relation (31) in this way: From the Table 1 it is seen that the percolation threshold can have different values, and, therefore, instead of $\dfrac{1}{3}$ the parameter g will be used. We rearrange relation (31) in the following form:

$$\sum_{n=1}^{N_1} c_n \frac{\lambda_n^* - \lambda_{\mathrm{eff}}}{(1-g)\lambda_{\mathrm{eff}} + g\lambda_n^*} + \sum_{n=N_1+1}^{N} c_n \frac{\lambda_n - \lambda_{\mathrm{eff}}}{(1-g)\lambda_{\mathrm{eff}} + g\lambda_n} = 0, \tag{36}$$

and further generalize it as follows:

$$c_1\frac{1-x^{\frac{1}{t}}}{(1-g)x^{\frac{1}{t}}+g}+\sum_{n=2}^{N_1}c_n\frac{r^{*\frac{1}{t}}-x^{\frac{1}{t}}}{(1-g)x^{\frac{1}{t}}+gr^{*\frac{1}{t}}}+ \\ +\sum_{n=N_1+1}^{N}c_n\frac{r^{\frac{1}{t}}-x^{\frac{1}{t}}}{(1-g)x^{\frac{1}{t}}+gr^{\frac{1}{t}}}=0, \tag{37}$$

where $x=\dfrac{\lambda_{\text{eff}}}{\lambda_1^*}$; $r_n^*=\dfrac{\lambda_n^*}{\lambda_1^*}$; $r_n=\dfrac{\lambda_n}{\lambda_1^*}$. In the generalization of Eq. (36) we exploited that $\lambda_{\text{eff}}=\lambda_2$ for $c=0$, $\lambda_{\text{eff}}=\lambda_1^*$ for $c=1$, $\lambda_{\text{eff}}=\lambda$, if $\lambda_n^*=\lambda_n=\lambda$ for arbitrary n and c and for $r=0$ $\lambda_{\text{eff}}\approx(c-g)^t$ (35). The above-mentioned requirements uniquely determine the generalized equation (37).

For the binary system, Eq. (37) simplifies

$$c\frac{1-x^{\frac{1}{t}}}{(1-g)x^{\frac{1}{t}}+g}+(1-c)\frac{r^{\frac{1}{t}}-x^{\frac{1}{t}}}{(1-g)x^{\frac{1}{t}}+gr^{\frac{1}{t}}}=0. \tag{38}$$

The solution of Eq. (38) is the following:

$$x=\left\{\frac{c(1-r^{\frac{1}{t}})+(1-g)r^{\frac{1}{t}}-g}{2(1-g)}+ \right. \\ \left. +\sqrt{\left[\frac{c(1-r^{\frac{1}{t}})+(1-g)r^{\frac{1}{t}}-g}{2(1-g)}\right]^2+\frac{g}{1-g}r^{\frac{1}{t}}}\right\}^t. \tag{39}$$

The computer simulations of the lattice models show that near to the percolation threshold (critical region) parameter t is equal approximately to 1.7 in the three dimensional case. The solution of Eq. (38) for $r=0$ is the following:

$$x=0, \quad c\leq g \tag{40}$$

and

$$x=\left(\frac{c-c_{\text{k}}}{1-g}\right)^t, \tag{41}$$

where $c_{\text{k}}=g$ is the percolation threshold. The computer simulations also show that for increasing c the parameter t is approaching 1. From this fact it follows that t is dependent on c.

Now we show for which condition the percolation, in a certain sense, may be observed. For this aim we find the value of c^* at which the second derivative of the function $x(c)$ has the maximum. For analytical calculations we put $t = 1$. From (39) it follows:

$$y^2 = \left[\frac{c(1-r)+(1-g)r-g}{2(1-g)}\right]^2 + \frac{g}{1-g}r, \tag{42}$$

where we have used

$$y = x - \frac{c(1-r)+(1-g)r-g}{2(1-g)}.$$

Differentiating equation (42) according to c one obtains

$$y\frac{\mathrm{d}y}{\mathrm{d}c} = \frac{1}{4}\frac{c(1-r)+(1-g)r-g}{(1-g)}\frac{1-r}{1-g}. \tag{43}$$

After the second and third differentiation of Eq. (43) we can write

$$\left(\frac{\mathrm{d}y}{\mathrm{d}c}\right)^2 + y\frac{\mathrm{d}^2x}{\mathrm{d}c^2} = \frac{1}{4}\left(\frac{1-r}{1-g}\right)^2. \tag{44}$$

$$3\frac{\mathrm{d}y}{\mathrm{d}c}\frac{\mathrm{d}^2x}{\mathrm{d}c^2} + y\frac{\mathrm{d}^3x}{\mathrm{d}c^3} = 0. \tag{45}$$

For $c = c^*$, from (45), it follows that

$$\left.\frac{\mathrm{d}y}{\mathrm{d}c}\right|_{c=c^*} = 0 \tag{46}$$

because we assume that $\left.\frac{\mathrm{d}^2x}{\mathrm{d}c^2}\right|_{c=c^*}$ is nonzero. Introducing (46) into (43) we get

$$c^* = \frac{g(1+r)-r}{1-r}. \tag{47}$$

Inequality $0 < c^* < 1$ implicates restrictions for the parameter r of the percolation-like behaviour of a composite system:

$$r < \frac{g}{1-g}, \quad r < \frac{1-g}{g}. \tag{48}$$

From (47) it follows: the smaller is r the better $c^* \approx g$ holds. If we denote c^* as the $g(1-\alpha)$, where α is considered as $\ll 1$, then

$$r = \frac{g\alpha}{1-g(2-\alpha)} \approx g\frac{\alpha}{1-2g},$$

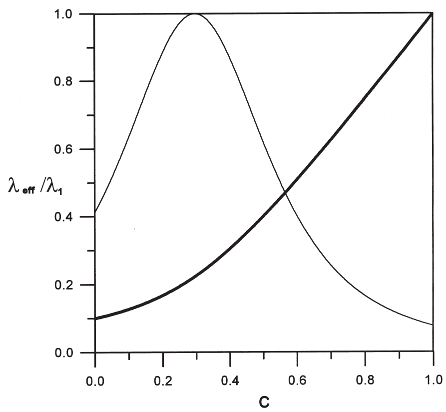

Fig. 3. Plot of $\frac{d^2x}{dc^2}$ and relative effective thermal conductivity vs. volume fraction of the filler, c; $r = 0.1$; thin line – $\frac{d^2x}{dc^2}$; thick line – $\frac{\lambda_{eff}}{\lambda_1}$.

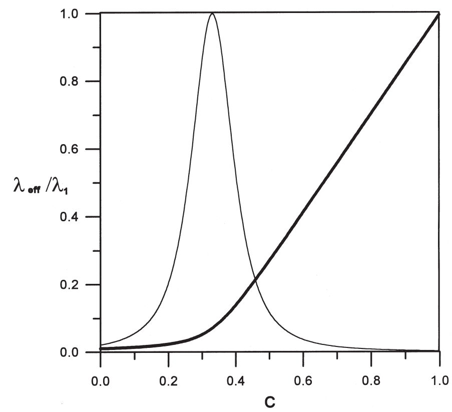

Fig. 4. Plot of $\frac{d^2x}{dc^2}$ and relative effective thermal conductivity vs. volume fraction of the filler, c; $r = 0.01$; thin line – $\frac{d^2x}{dc^2}$; thick line – $\frac{\lambda_{eff}}{\lambda_1}$.

where relation (47) was used. From (47) it follows that for $g = \frac{1}{3}$ and $r = \frac{1}{2}$ the parameter $c^* = 0$. But for $g = \frac{1}{3}$ and $r < \frac{1}{2}$ the parameter $c^* > 0$. In Figs. 3 and 4 the plots of x and $\frac{d^2x}{dc^2}$ vs. c for $g = \frac{1}{3}$ and $r = 0.1;\ 0.01$ are depicted. According to relation (47) for $g = \frac{1}{3}$ and $r = 0.1$, the value of c^* is equal to $\frac{1}{3}0.89$ and for $r = 0.01$ $c^* = \frac{1}{3}0.99$. From that we see that the smaller is r the nearer is to the percolation threshold c^*. The plot of $\frac{d^2x}{dc^2}$ is asymmetric according to c^* what means that at the percolation phase transition (percolation threshold) the dependence of x on c changes. In [9] and [10] relation (39) was tested according to experimental data. The parameters g and t were considered as free parameters which were determined from experiment. It was shown that formula (39) describes the experimental results quite well. The parameter t was considered as independent of c. In Fig. 5 are shown the plots of x on c at $g = \frac{1}{3}$, $t = 1$ and $t = 1 + \frac{T-1}{g(1-g)}c(1-c)$. The form of the function $t(c)$ was determined from the conditions: $t = 1$ at $c = 0$ and $c = 1$; $t = T$ at $c = g$. The thin curve corresponds to $r = 0.01$, $t = 1$ and $g = \frac{1}{3}$, the thick one to

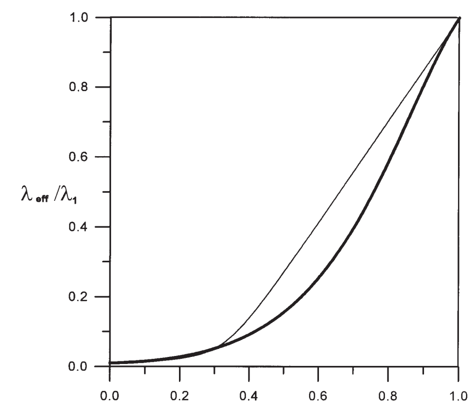

Fig. 5. Relative effective thermal conductivity vs. volume fraction of the filler, c; thin line – $t = 1$; thick line – $t = 1 + \frac{T-1}{g(1-g)}c(1-c)$.

$r = 0.01$, $g = \frac{1}{3}$ and $T = 1.7$. The value of the parameter T was chosen so that in the critical region (near to percolation threshold) $t = 1.7$ as it is seen from Table 1.

The mean field approximation method, as we mentioned, is approximate. It gives only the basic form of the relation for the effective thermal conductivity. Further improvement can be done by a generalization of the formula (36), which would describe better the dependence of the thermal conductivity on the volume fraction of the filler. Therefore, the generalized formula (39) has to be tested for experimental data. After the successful test it may be used by the technologist for design of composition of novel composite materials, which would meet the application requirements.

5. Conclusion

– The formula for the effective thermal conductivity of particulate composite with coated granules of certain components was derived.

– The formula was generalized by introducing the parameter t which is dependent in the case of binary system on the volume fraction of the filler.

– In the case of a binary system an analysis of the obtained results was performed.

– It was shown that the $\frac{d^2x}{dc^2}$ has the maximum for certain value of the volume fraction c^*. The value of c^* is near to the percolation threshold if certain conditions are fulfilled.

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