Int J Thermophys (2010) 31:975–986
DOI 10.1007/s10765-010-0756-2

Generalized Bruggeman Formula for the Effective Thermal Conductivity of Particulate Composites with an Interface Layer

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Received: 16 June 2009 / Accepted: 13 May 2010 / Published online: 30 May 2010

Abstract Combining the well-known Bruggeman theory and Nan et al. results, formulas for predicting the effective thermal conductivity of anisotropic particulate composites with an interface layer are derived. These formulas are valid for a composite material containing arbitrarily oriented ellipsoidal particles with any aspect ratio, and they can be expected to be suitable mainly for large volume fractions, when the thermal interaction between neighboring particles needs to be considered. Results of the present approach are reduced to simpler formulas for some limiting cases in the particle shape. Theoretical analysis of the effective thermal conductivity as a function of volume fraction and shape of the particles is performed. Comparison of the obtained formulas with previously reported experimental data for the effective thermal conductivity is also presented.

Keywords Bruggeman theory · Coated particles · Composite materials · Effective thermal conductivity · Nan formula

1 Introduction

Composites materials have always attracted great interest, due to the fact that they can inherit the desirable properties of its components while enhancing others. The

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properties of the composites depend on the dimensions, geometry, physical properties, concentration, and interactions of the particles and matrix. The prediction and understanding of the properties of these materials are a complex subject in which the analysis of the macroscopic properties is performed in base to effective theories. A variety of useful formalisms have been developed, in particular, the pioneering work of the Maxwell approach based on an electrostatic analogy with thermal phenomena [1,2]. However, it has been claimed recently that in the case of nanofluids in which a small quantity of very small particles (some nanometers in size) in a fluid matrix, very high thermal conductivities can be obtained [3,4].

In order to explain these results, different approaches have been developed; for a summary on the conventional models of the effective thermal conductivity of two-phase composites, the reviews by Choi et al. [3] and Wang et al. [5], and the book by Das et al. [6] are recommended. Based on experimental results, various mechanisms and models have been proposed to understand this anomalous enhancement of the thermal conductivity. The convection caused by the Brownian motion of nanoparticles was proposed as one of the physical mechanisms [7], the effect of the matrix–particles interface has been explored [8], and the effects of the shape of the particles have been shown to play an outstanding role. One of the most interesting approaches was developed by Nan et al. [9], which generalized the Maxwell–Garnett approximation to derive a simple formula for the effective thermal conductivity of ellipsoidal-particle composites. The magnitude of the large thermal conductivity enhancement observed in some experiments was well predicted within this approach. However, this model cannot explain some of the experimental data, including phenomena in which that the effective thermal conductivity of nanotube suspensions is nonlinear with nanotube volume fractions [3,9]. A common situation found in particulate composite materials is such that the particles are coated, or show an interface between the particles and the surrounding medium, in this case, different approaches have been developed considering the thermal interface resistance [6,10]; however, it would be desirable to have at hand a formulation with the minimum number of free parameters and with the possibility of considering high conductivity particle coatings.

In this article, the thermal conductivity of a composite material formed by ellipsoidal particles coated with a shell of fixed thickness is studied. The analysis is performed using the differential effective medium (DEM) theory, based on the Bruggeman integration principle, taking into account both the geometric anisotropy and the interface effects. It is shown that it is possible to obtain [11] an effective thermal conductivity valid at a high volume fraction of particles as well as at low concentrations of particles. For randomly isotropic spherical inclusions without interface thermal resistance, our formula reduces to the well-known result proposed by Bruggeman [11]. An analysis of the prediction of the effective thermal conductivity based on the particulate shape and interface effects is presented. It is shown that even for extremely low volume fractions, our results predict the nonlinear relation between the effective thermal conductivity and the volume fraction [4,12–14]. Comparisons of our theoretical results with experimental data are presented.

2 DEM Theory

The DEM theory was first introduced by Bruggeman [11] and can be used to estimate the effective thermal conductivity of composites at high particle concentrations [1,11,15]. It consists in building up the composite medium through a process of incremental homogenization. In our case, particles with thermal conductivity k_p, each one surrounded by a shell of thermal conductivity k_s and embedded in a matrix of thermal conductivity k_m (Fig. 1a) are considered. Let us suppose that this matrix can be treated as a homogeneous medium with an effective thermal conductivity $k(f)$ (Fig. 1b), with f being the volume fraction of the particles. The effective conductivity can then be assumed to be given by

$$k(f) = k_m[1 + A(k_m, k_p, k_s)f + B(k_m, k_p, k_s)f^2 + \cdots], \tag{1}$$

where the dimensionless coefficient $A(k_m, k_p, k_s)$ determines the behavior of the effective thermal conductivity in the dilute limit ($f \ll 1$, such that the particles do not interact among themselves) and may also depend on the shape of the particles, and $B(k_m, k_p, k_s)$ takes into account the first-order correction to the dilute limit and the contribution of particle interactions, possibly. The higher-order coefficients of f are strongly related with the interactions among the particles, and they can be neglected in the dilute limit.

Now assume that a volume element ΔV is removed from the homogeneous medium (Fig. 1b) and is replaced by an equivalent volume of particles. In this way, the

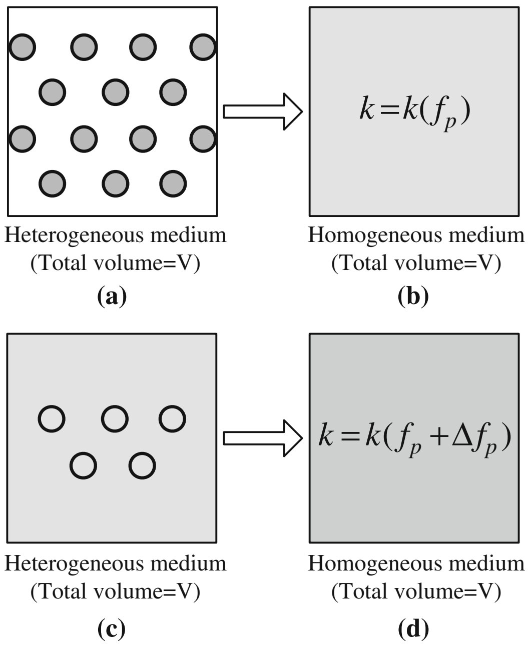

Fig. 1 Schematic view of the process of incremental homogenization of the DEM theory

homogeneous medium can be treated as the new matrix and the effective thermal conductivity $k(f + \Delta f)$ of the new homogeneous medium (Fig. 1d) is given by (see Eq. 1)

$$k(f + \Delta f) = k(f)\left[1 + A(k(f), k_{\mathrm{p}}, k_{\mathrm{s}})\frac{\Delta V}{V} + B(k(f), k_{\mathrm{p}}, k_{\mathrm{s}})\left(\frac{\Delta V}{V}\right)^2 + \cdots\right], \tag{2}$$

where $\Delta f = (\Delta V - \Delta V_{\mathrm{p}})/V$ is the net increase of the volume fraction of particles, with ΔV_{p} being the volume of particles that has been removed. For the homogeneous medium, we have that on average $\Delta V_{\mathrm{p}}/V_{\mathrm{p}} = \Delta V/V$, with V_{p} being the volume of particles in the initial system (Fig. 1a). In this way, $\Delta V/V = \Delta f/(1 - f)$ and Eq. 2 can be written as:

$$\frac{k(f + \Delta f) - k(f)}{\Delta f} = \frac{k(f)}{1 - f}\left[A(k(f), k_{\mathrm{p}}, k_{\mathrm{s}}) + B(k(f), k_{\mathrm{p}}, k_{\mathrm{s}})\frac{\Delta f}{1 - f} + \ldots\right]. \tag{3}$$

In the limit $\Delta f \to 0$, Eq. 3 becomes in the differential equation

$$\frac{\mathrm{d}k}{\mathrm{d}f} = \frac{k}{1 - f}A(k, k_{\mathrm{p}}, k_{\mathrm{s}}), \tag{4}$$

which can be integrated, under the condition $k(f = 0) = k_{\mathrm{m}}$ to yield

$$\int_{k_{\mathrm{m}}}^{k} \frac{\mathrm{d}k}{kA(k, k_{\mathrm{p}}, k_{\mathrm{s}})} = -\ln(1 - f), \tag{5}$$

which is the most important result of the DEM theory and establishes that the effective thermal conductivity of a composite with an arbitrary volume fraction of particles ($f < 1$) can be found using the dilute limit of Eq. 1. In this way, a formula for the effective thermal conductivity that is valid at low concentrations of particles can be used to generate a new formula valid for high concentrations as well as for low volume fraction of particles.

It is important to note that the DEM theory is only valid when the process of incremental homogenization can be performed [1]. This can be suitably done for polydisperse inclusions in shape and size, or at least in size [1,9], in such a way that the particles have a distribution of sizes from small to large and they do not form large clusters [1]. Given that in the most practical applications the particles are not monodisperse but rather have dispersion in their geometry, the DEM theory is expected to be suitable in such cases. From now on, inclusions with the same ellipsoidal shape and different sizes are going to be considered.

Considering composites in which randomly oriented ellipsoidal particles of thermal conductivity k_{p}, each one surrounded by a interface layer of thermal conductivity k_{s} are

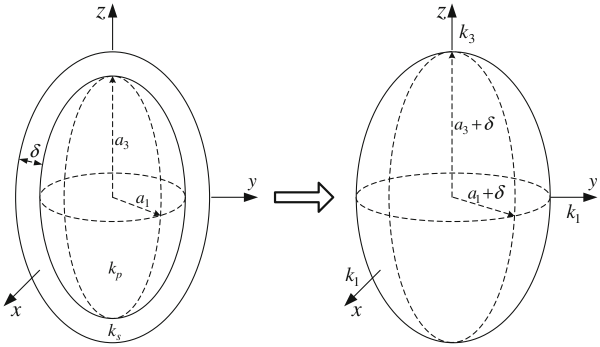

Fig. 2 Mapping of a real ellipsoidal particle with a surrounding layer into an effective particle

embedded in a matrix with thermal conductivity k_{m}, according to Nan et al. [9] results, the real particle can be represented by an effective particle (see Fig. 2) with thermal conductivities k_1 and k_3 along the transverse and longitudinal axes, respectively, given by

$$k_i = k_{\mathrm{s}}\left[1+\frac{\upsilon(k_{\mathrm{p}}-k_{\mathrm{s}})}{k_{\mathrm{s}}+L_i(k_{\mathrm{p}}-k_{\mathrm{s}})(1-\upsilon)}\right], \quad i=1,3; \tag{6}$$

where,

$$\upsilon = \left(\frac{a_1}{a_1+\delta}\right)^2\left(\frac{a_3}{a_3+\delta}\right), \tag{7a}$$

$$L_1 = \begin{cases} \frac{p^2}{2(p^2-1)} - \frac{p}{2(p^2-1)^{3/2}}\cosh^{-1}(p), & p>1, \\ \frac{p^2}{2(p^2-1)} + \frac{p}{2(1-p^2)^{3/2}}\cos^{-1}(p), & p<1, \end{cases} \tag{7b}$$

$$L_3 = 1-2L_1, \tag{7c}$$

with a_1 and a_3 being the average radii of the geometrical distribution of the ellipsoidal particles along the transverse and longitudinal local axes, respectively, δ is the average thickness of the surrounding interface layer, and $p = a_3/a_1$ is the eccentricity of the ellipsoids. It is important to note that Eq. 6 is only valid for isotropic particles, in such a way that their thermal conductivity can be represented by the single parameter k_{p} in all directions, at least, as an average. If the thermal conductivity of the particles varies remarkably with the direction, Eq. 6 is no longer valid [9]. For this reason, all the inclusions are going to be considered isotropic.

Since the embedded ellipsoidal particles are randomly oriented, the composite is isotropic and therefore its effective thermal conductivity k is the same in all directions, and it would depend on a single parameter given by [9]

$$\frac{k}{k_{\mathrm{m}}} = \frac{3+[2\beta_1(1-L_1)+\beta_3(1-L_3)]\,f_{\mathrm{p}}}{3-[2\beta_1 L_1+\beta_3 L_3]\,f_{\mathrm{p}}}, \tag{8}$$

where

$$\beta_i = \frac{k_i - k_\mathrm{m}}{k_\mathrm{m} + L_i(k_i - k_\mathrm{m})}, \quad i = 1, 3. \tag{9}$$

It has been shown that Eq. 8 predicts successfully the thermal conductivity of composite materials, especially for low volume fractions of particles [9]. In order to obtain a better estimation of the thermal conductivity of the composite with high concentrations of particles, Eqs. 5 and 8 can be combined. By giving Eq. 8 the form of Eq. 1, it can be shown that the coefficient A can be expressed as

$$A = \frac{2\beta_1 + \beta_3}{3} \tag{10}$$

After replacing Eq. 10 in 5 with the substitution $k_\mathrm{m} \to k$, and carrying out the corresponding integration, it is obtained;

$$\left(\frac{k}{k_\mathrm{m}}\right)^{3B} \left(\frac{k - k_+}{k_\mathrm{m} - k_+}\right)^{3B_+} \left(\frac{k - k_-}{k_\mathrm{m} - k_-}\right)^{3B_-} = 1 - f, \tag{11}$$

where

$$B = \frac{L_1 L_3}{3L_1 - 2}, \tag{12a}$$

$$B_\pm = \pm \frac{\left[(1 - L_1)k_\pm + L_1 k_1\right]\left[(1 - L_3)k_\pm + L_3 k_3\right]}{D k_\pm}, \tag{12b}$$

$$k_\pm = \frac{3L_1 k_1 + (3L_1 - 1)k_3 \pm D}{2(3L_1 + 1)}, \tag{12c}$$

$$D = \sqrt{9L_1^2 k_1^2 + (3L_1 - 1)^2 k_3^2 + 2\left(4 + 3L_1 - 9L_1^2\right) k_1 k_3}. \tag{12d}$$

In this way, Eq. 11 takes into account the effects, not only of the volume fraction of particles, but also of their size, shape, and surrounding interface layer. For spherical particles, $p = 1$, $L_1 = L_3 = 1/3$, and $k_1 = k_3 \equiv k_\mathrm{ps}$; then Eq. 11 reduces to

$$\left(\frac{k_\mathrm{m}}{k}\right)^{1/3} \left(\frac{k - k_\mathrm{ps}}{k_\mathrm{m} - k_\mathrm{ps}}\right) = 1 - f. \tag{13}$$

In absence of the surrounding interface layer, $\upsilon = 1$, $k_\mathrm{ps} = k_\mathrm{p}$, and Eq. 13 reduces to the classical Bruggeman formula [11]. In this way, Eq. 11 represents the generalization of the Bruggeman formula when the particles have a surrounding interface layer that interacts directly with the matrix. Notice that after rewriting Eq. 13 as a third-degree polynomial, an analytical expression can be obtained for the effective thermal conductivity.

For ellipsoidal particles without a surrounding interface layer ($\upsilon = 1$), Eq. 11 reduces to

$$\left(\frac{k}{k_{\rm m}}\right)^{b}\left(\frac{k-k_{\rm p}}{k_{\rm m}-k_{\rm p}}\right)\left(\frac{k-k_0}{k_{\rm m}-k_0}\right)^{c}=1-f, \tag{14}$$

where

$$b=\frac{3L_3(L_3-1)}{3L_3+1}, \tag{15a}$$

$$c=\frac{2(3L_3-1)^2}{(3L_3-5)(3L_3+1)}, \tag{15b}$$

$$k_0=\frac{(3L_3+1)k_{\rm p}}{3L_3-5}. \tag{15c}$$

Considering the extreme geometrical shapes of an ellipsoid, two particular cases of Eq. 14 are considered:

- For random-oriented long cylindrical particles, $p \to \infty$ and $L_3 = 0$; therefore, Eq. 14 reduces to

$$\left(\frac{k-k_{\rm p}}{k_{\rm m}-k_{\rm p}}\right)\left(\frac{5k+k_{\rm p}}{5k_{\rm m}+k_{\rm p}}\right)^{-2/5}=1-f, \tag{16}$$

  which can be solved numerically for the effective thermal conductivity k.
- For random-oriented laminated flat particles, $p \to 0$ and $L_3 = 1$, then Eq. 14 reduces to

$$\left(\frac{k-k_{\rm p}}{k_{\rm m}-k_{\rm p}}\right)\left(\frac{k_{\rm m}+2k_{\rm p}}{k+2k_{\rm p}}\right)=1-f, \tag{17}$$

  which can be solved analytically for the effective thermal conductivity k.

3 Numerical Results

In this section, the predictions of the obtained equations for the effective thermal conductivity are presented and analyzed. To understand the effect of the particle shape, the normalized effective thermal conductivity $k/k_{\rm m}$ has been studied as a function of the shape factor L_3 for three values of the ratio $k_{\rm p}/k_{\rm m}$, volume fraction $f = 0.2$ and particles without a surrounding interface layer ($\upsilon = 1$). The results are shown in Fig. 3, in which it can be observed that the effective thermal conductivity increases for either small ($L_3 \to 0$) or large ($L_3 \to 1$) values of the shape factor and takes its minimum value when $L_3 = 1/3$, which corresponds to spherical particles. This can be understood taking into account that particles with shapes remarkably different from a sphere have a large aspect ratio (the ratio of its longer dimension to its shorter

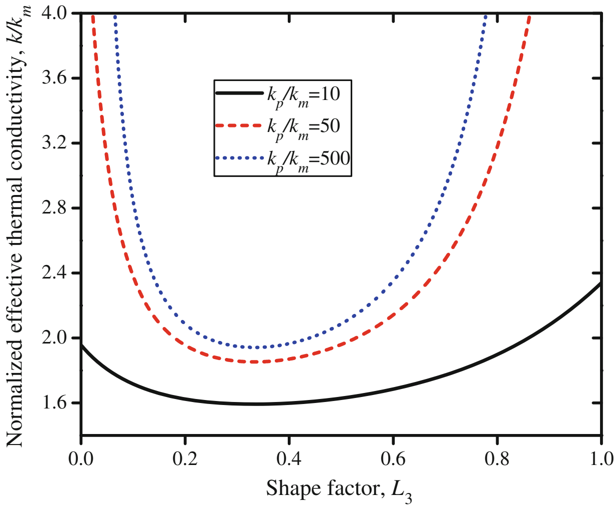

Fig. 3 Normalized effective thermal conductivity as a function of the shape factor L_3 at a volume fraction of particles $f = 0.2$

one), providing a better thermal conduction path than the one presented by a sphere and therefore a larger thermal conductivity.

In Fig. 4, the normalized effective thermal conductivity as a function of the volume fraction of particles is shown for three values of the shape factor L_3, taking $k_\mathrm{p}/k_\mathrm{m} = 50$ and considering that there is not a surrounding interface layer ($\upsilon = 1$). It can be observed that for prolate particles ($L_3 < 1/3$) the effective thermal conductivity is larger than that for spherical particles ($L_3 = 1/3$) but is smaller than that for oblate particles ($L_3 > 1/3$). In this way, the shape of the particles plays an important role in the enhancement of the effective thermal conductivity.

In Fig. 5a and b, for the case of spherical particles, the normalized effective thermal conductivity as a function of the volume fraction of particles is shown for three values of the ratio (δ/a) between the thickness (δ) of the surrounding interface layer and the radius (a) of the spherical particles. Calculations were performed taking $k_\mathrm{s}/k_\mathrm{m} = 5(k_\mathrm{p}/k_\mathrm{s} = 10$ in Fig. 5a and $k_\mathrm{p}/k_\mathrm{s} = 0.1$ for Fig. 5b) and using Eq. 13. In Fig. 5a, it can be observed that the effective thermal conductivity decreases when the ratio δ/a increases. This is due to the fact that in this case $k_\mathrm{p} > k_\mathrm{s}$. On the other hand, for $k_\mathrm{p} < k_\mathrm{s}$; Fig. 5b shows that the effective thermal conductivity increases when the ratio δ/a does, such as was expected.

In Fig. 6, it can be observed that under the conditions $\delta/a = 1/5$, and $k_\mathrm{p} = k_\mathrm{m} = 5\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$; the normalized effective thermal conductivity increases when the particle shell thermal conductivity k_s does. This increment is more remarkable for high volume fractions of the spherical particles. This fact could be used for building up materials made of low thermal conductivity particles and a matrix (and therefore of low cost) by means of their coatings with a shell of high thermal conductivity.

In order to compare our approach with real experimental data, in Fig. 7 the behavior predicted by our model (Eq. 13) with the measured values reported by

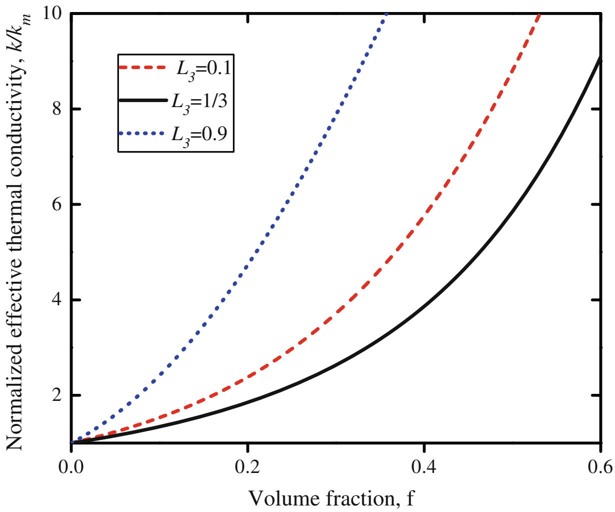

Fig. 4 Normalized effective thermal conductivity as a function of the volume fraction of particles, for three values of the shape factor L_3 and taking $k_p/k_m = 50$

Krupa et al. [16] are shown. The system consisted of spherical polyamide particles ($k_p = 0.24\,\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) coated with a silver shell ($k_s = 430\,\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) embedded in a matrix of high-density polyethylene ($k_m = 0.45\,\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). An average value of $\delta/a = 0.6$ was reported. As can be observed, the system exhibits a nonlinear increase of k/k_m with the volume fraction of particles. Notice that for low concentrations ($f < 0.1$), the predictions of Eq. 13 are in good agreement with the experimental results; however, there is a discrepancy between them at higher concentrations ($f > 0.1$). This could be due to the fact that the reported system consists of polydisperse particles [16], which mean that the ratio δ/a is not fixed, such as is required by Eq. 13. Additional effects could be related to the interaction among the particles with the coating and the matrix. These effects become more important for high volume fractions of particles.

Our approach can also be applied to an additional system formed by spherical iron particles with thermal conductivity $k_p = 74\,\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ inside a liquid silicone matrix with thermal conductivity $k_m = 0.15\,\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [17]. The thermophysical characterization was performed using the highly sensitive technique known as thermal waves resonator cavity [17]. The predictions of Eq. 13 and the experimental data reported by Medina et al. [18] are shown in Fig. 8. It can be observed that very good agreement is obtained in this case. The fitting of the experimental data results with our formula is better than in the case presented in Fig. 6, due to the better distribution of the particle shapes and sizes, and better thermal contact between fluid matrix and particles.

4 Conclusions

Based on Bruggeman DEM theory and Nan et al. results, a general formula to predict the effective thermal conductivity of anisotropic particulate composites with an

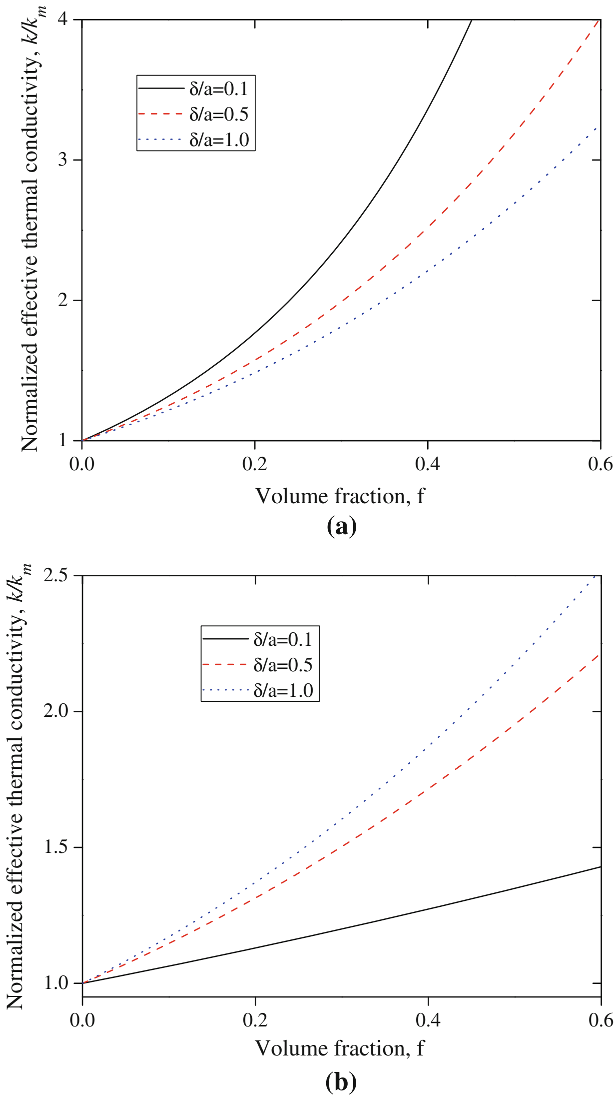

Fig. 5 Normalized effective thermal conductivity as a function of the volume fraction of spherical particles, for three values of the ratio δ/a and taking $k_s/k_m = 5$ and (**a**) $k_p/k_s = 10$ and (**b**) $k_p/k_s = 0.1$

interface layer has been obtained. This result reduces to simpler formulas for some limiting cases in the particle shape and thickness of the interface layer. Considering randomly oriented ellipsoidal particles, it is numerically shown that for prolate particles the effective thermal conductivity is larger than that for spherical particles but it is smaller than that of oblate particles. It is found that the thickness and thermal conductivity of the interface layer play a determinant roll in the enhancement of the effective thermal conductivity. The predictions of our formula for the effective thermal

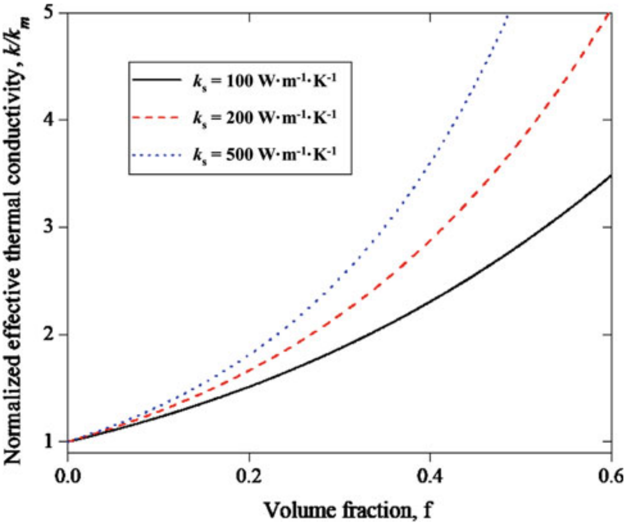

Fig. 6 Normalized effective thermal conductivity as a function of the volume fraction of spherical particles, for three values of particle shell thermal conductivity k_S. Calculations have been performed taking $\delta/a = 1/5$ and $k_p = k_m = 5\,W \cdot m^{-1} \cdot K^{-1}$

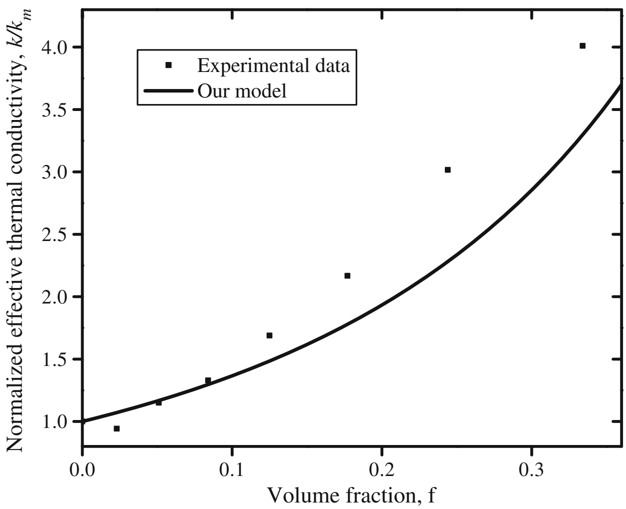

Fig. 7 Comparison between numerical predictions and reported experimental data for the normalized effective thermal conductivity as a function of the volume fraction of polyamide particles coated by a silver shell and embedded in a matrix of high-density polyethylene

conductivity of spherical polyamide particles coated by a silver shell and embedded in a matrix of high-density polyethylene are in good agreement with the experimental results, for low concentrations. In addition, good agreement between our theoretical results and experimental data for hard iron particles embedded in a matrix of silicone oil has been shown.

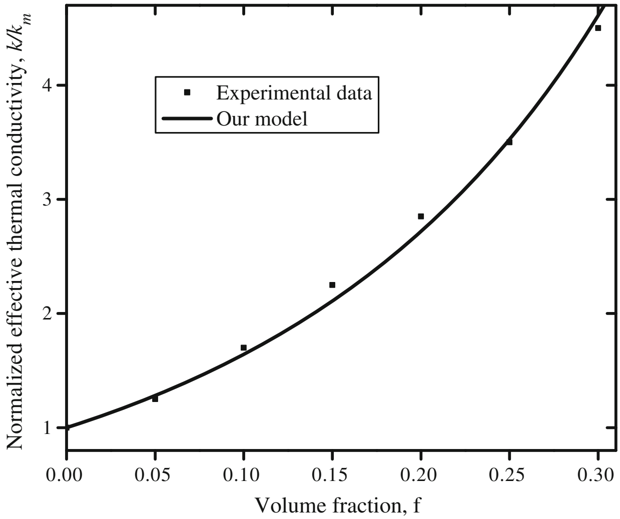

Fig. 8 Comparison between numerical predictions and experimental data for the normalized effective thermal conductivity as a function of the volume fraction of hard iron particles embedded in a matrix of silicone oil

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