Journal of Physics D:
Applied Physics

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To cite this article: Liisi Jylhä and Ari Sihvola 2007 *J. Phys. D: Appl. Phys.* **40** 4966

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IOP Publishing Journal of Physics D: Applied Physics
J. Phys. D: Appl. Phys. **40** (2007) 4966–4973 doi:10.1088/0022-3727/40/16/032

Equation for the effective permittivity of particle-filled composites for material design applications

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Received 9 May 2007, in final form 20 June 2007
Published 3 August 2007
Online at stacks.iop.org/JPhysD/40/4966

Abstract
A new simple equation for the effective permittivity of particle-filled composites is presented. The equation does not involve any free parameters in addition to the volume fraction of inclusions, the semi-axes of ellipsoidal inclusions and the permittivities of materials. Alternatively, instead of semi-axes, the percolation threshold can be used as a parameter. It is derived in a similar manner as the Maxwell Garnett mixing equation, but by including an enhanced background permittivity effect when the volume filling ratio of inclusions increase. The result is a mixing equation which has the Maxwell Garnett mixing equation as a low volume filling ratio limit, but which approaches the Bruggeman mixing equation as the volume fraction of inclusions increases. The mixing equation is compared with classical mixing formulae, and to numerical simulations and measurements from the literature.

1. Introduction

In many composite material engineering problems, the aim is to design a material with desired electrical and mechanical properties. The free parameters with which one can affect the macroscopic properties of the composite are the properties of the individual phases, their relative fractional volumes and the shapes of the inclusions. In figure 1 an illustration of an engineered material is presented. There black inclusions with permittivity ε_i are randomly dispersed into a white background with permittivity ε_e. To highlight the possibility that the composite can be completely filled with black inclusions, the boundaries between white inclusions are marked. The illustration corresponds, for example, to a composite that is constructed by compressing two ceramic powders. However, in the case of ceramic–polymer composites, there would be no boundaries between white inclusions.

Classical mixing formulae, like Maxwell Garnett or Bruggeman, are widely used to calculate the effective permittivity of such mixtures. There are areas of application where these formulae work very well. For example, in the area of remote sensing, the contrast between the permittivities of the various phases of the heterogeneous structures is not very large. In that case both Maxwell Garnett and Bruggeman mixing formulae predict reasonably accurate results.

However, in the case of applications to material engineering, the effective permittivity often needs to be as large as possible. On the other hand, sometimes the composite needs to be constructed with a polymer matrix because of desired mechanical properties. Then the electrical contrast between the phases may be extremely large, even several thousands. Such examples arise in the design of embedded capacitors and LTCC technology [1,2]. In addition, the volume filling ratio of ceramic inclusions varies from very dilute composites to composites where the ceramic loading is as high as possible. The combination of highly packed inclusions with high electrical contrast leads to a situation where two mixing equations should be used simultaneously. If the effective permittivity of the composite is measured as a function of the volume fraction of ceramic powder in the polymer background, there are several good methods to fit a semi-empirical model to the measurement result [3–6]. However, if the effective permittivity of the composite needs to be predicted in order to find general principles for how to choose the best material combination for the given application, the choice of the mixing theory is problematic. Another shortcoming of the semi-empirical models is that the parameters do not describe separate

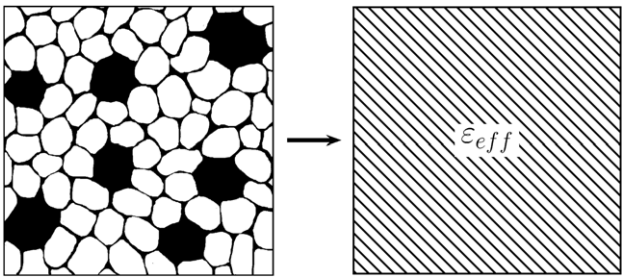


Figure 1. Homogenization of a two phase mixture of black inclusions with permittivity ε_i in background with ε_e.

physical properties of the mixture. For example, if one parameter is responsible for the percolation threshold of the mixture, a change in this parameter also changes the low volume filling ratio properties of the mixture. The effective permittivity of the composite with very low-filling ratios of spheres is dominated by the shape of inclusions. As a result, the percolation parameter is also dependent on the shape of inclusions.

In addition to classical mixing equations (Maxwell Garnett or Bruggeman) for random composites there are accurate electromagnetic solutions for ordered composites [7–10]. In [11] close-packed random mixtures are studied. In the case of ceramic/ceramic composites, the volume filling ratio of inclusions can be freely chosen. It does not have any upper limit. But the arrangement is often more random than ordered. Formulae that are derived for ordered lattices are not applicable in the whole range of volume filling ratios of inclusions because they have an asymptotic behaviour at the volume filling ratio where inclusions inside unit cells touch the cell boundaries.

The aim of this study is to derive and present an easy-to-use mixing formula for material engineering applications, which combines the low volume filling ratio properties of the Maxwell Garnett mixing equation to the percolation properties of the Bruggeman mixing equation. The equation does not involve any adjustable free parameters and the derivation is based on the electromagnetic analysis. The needed parameters are the shape of inclusions, the volume fraction of inclusions and the permittivities of the matrix and of the inclusions. The new mixing equation predicts very accurately the effective permittivity as a function of volume fraction of inclusions, in the case where the shape of inclusions can be modelled as ellipsoids and they are evenly distributed.

For example, if the effective permittivity of a polymer/ceramic composite needs to be maximized with a minimum amount of ceramic particles, the equation presented in this paper would be very useful. Typically for this kind of application high-permittivity ceramic inclusions are chosen, but the permittivity of the polymer matrix is low. (High-permittivity polymers already have embedded ceramic inclusions and therefore they cannot be used without high total volume fraction of ceramic.) The permittivity would increase either by increasing the amount of ceramic inclusion in the composite or by choosing shapes for inclusions that are as far away from spherical as possible. If one tries to use semi-empirical models, the problem is how to choose the adjustable parameters that are not known for that given material combination. If one tries to use classical mixing equations that have a solid electromagnetic basis and no matching parameters, the optimal material combination is very hard to predict. With small volume filling fractions of ceramic, the Maxwell Garnett mixing equation should be used, because it takes the effect of the shape of inclusions correctly into account. When approaching the percolation threshold, one should switch to the Bruggeman equation. This problem does not exist with the use of the new mixing equation.

The outline of the paper is as follows. At first classical mixing formulae for random composites are introduced. In the next section the new equation is derived and then its mathematical validation is discussed. Finally, the equation is compared with classical mixing equations, numerical simulations and experimental results found from the literature.

Table 1. Classical mixing formulae for random orientation of inclusions.

$\varepsilon_{\text{eff}} = \varepsilon_e + \varepsilon_e \dfrac{\frac{f}{3}\sum_{j=x,y,z} \dfrac{\varepsilon_i - \varepsilon_e}{\varepsilon_e + N_j(\varepsilon_i - \varepsilon_e)}}{1-\frac{f}{3}\sum_{j=x,y,z} \dfrac{N_j(\varepsilon_i - \varepsilon_e)}{\varepsilon_e + N_j(\varepsilon_i - \varepsilon_e)}}$	(MG)
$\varepsilon_{\text{eff}} = \varepsilon_e + \frac{f}{3}(\varepsilon_i - \varepsilon_e) \sum_{j=x,y,z} \dfrac{\varepsilon_{\text{eff}}}{\varepsilon_{\text{eff}} + N_j(\varepsilon_i - \varepsilon_{\text{eff}})}$	(BS)
$\varepsilon_{\text{eff}} = \varepsilon_e + \varepsilon_{\text{eff}} \dfrac{\frac{f}{3}\sum_{j=x,y,z} \dfrac{\varepsilon_i - \varepsilon_e}{\varepsilon_{\text{eff}} + N_j(\varepsilon_i - \varepsilon_e)}}{1-\frac{f}{3}\sum_{j=x,y,z} \dfrac{N_j(\varepsilon_i - \varepsilon_e)}{\varepsilon_{\text{eff}} + N_j(\varepsilon_i - \varepsilon_e)}}$	(CP)
$\dfrac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i - \varepsilon_e} = (1-f)\left(\dfrac{\varepsilon_{\text{eff}}}{\varepsilon_e}\right)^{1/3}$	(BN)
$\dfrac{\varepsilon_{\text{eff}} - \varepsilon_e}{\varepsilon_i - \varepsilon_e} = f\left(\dfrac{\varepsilon_{\text{eff}}}{\varepsilon_i}\right)^{1/3}$	(SSC)
$\varepsilon_{\text{eff}}^{1/3} = (1-f)\varepsilon_e^{1/3} + f\varepsilon_i^{1/3}$	(LO)
$\log\varepsilon_{\text{eff}} = f\log\varepsilon_i + (1-f)\log\varepsilon_e$	(LI)

2. Classical mixing formulae

In figure 1, material with permittivity ε_i and the volume filling fraction f is mixed with material with permittivity ε_e and volume fraction $1-f$. The basic idea behind all classical mixing formulae is to try to define and estimate the effective permittivity ε_{eff} for this mixture with the assumption that the scale of inhomogeneities is much smaller than the wavelength in the material.

If the shape of the inclusions can be modelled as spheres or ellipsoids, several mixing rules are provided by the literature. Table 1 lists existing and common mixing rules for the effective permittivity. There f is the volume filling fraction of the inclusion spheres or ellipsoids in the mixture, ε_i is the permittivity of the inclusions and ε_e is the permittivity of the background. The depolarization factors of the inclusion ellipsoids are denoted by $N_{x,y,z}$. For spheres these are $N_x = N_y = N_z = 1/3$. The depolarization factors for general ellipsoids contain elliptic integrals [12] but for spheroids,

closed-form expression can be written: for prolate spheroids ($a_z > a_x = a_y$), the depolarization factors are

$$N_z = \frac{1-e^2}{2e^3}\left(\ln\frac{1+e}{1-e} - 2e\right), \qquad N_x = N_y = \tfrac{1}{2}(1-N_z), \tag{1}$$

where the eccentricity is $e = \sqrt{1-a_x^2/a_z^2}$. For oblate spheroids ($a_z < a_x = a_y$),

$$N_z = \frac{1+e^2}{e^3}\left(e - \tan^{-1} e\right), \qquad N_x = N_y = \tfrac{1}{2}(1-N_z), \tag{2}$$

where $e = \sqrt{a_x^2/a_z^2 - 1}$, with a_x, a_y and a_z being the three semi-axes of the ellipsoid. Depolarization factors for any ellipsoid satisfy $N_x + N_y + N_z = 1$.

In the classical Maxwell Garnett mixing rule (MG) it is assumed that the local electric field on each ellipsoid is a superposition of the average external field and the average field caused by other spheres. The result for the effective permittivity is also known as the Clausius–Mossotti equation.

Another famous mixing formula for a similar mixture is the symmetric Bruggeman (Polder–van Santen) formula (BS) [13–15]. As the name suggests, it assumes a symmetry between inclusion and background phases. It is derived for small volume fractions of inclusions like the Maxwell Garnett equation. Coherent potential (CP) [16,17] is a third mixing rule which has the same behaviour with MG and BS for low-filling ratios of the ellipsoid-shaped inclusion phase.

Another class of mixing formulae is derived with differential analysis. They share the common property that the permittivities are raised to powers of one-third. Four differential-based formulae are given in the table: Bruggeman non-symmetric (BN) [13], Sen–Scala–Cohen (SSC) [18], Looyenga (LO) [19] and Lichtenecker (LI) [20,21]. In [22] it is shown that if the basic MG or symmetric Bruggeman rules are used in an iterative scheme, the result leads to the non-symmetric Bruggeman case. In addition to mixing rules in the table, there are also mixing formulae which contain adjustable parameters (see, for example, [3, 5, 6]) and homogenization theories for periodic arrays (see for example [7–10]), but those are not in the focus of this paper.

3. New differential mixing equation

In this section, the main result of the present paper is derived: a new mixing equation that combines the desired properties of MG and BS mixing rules. For simplicity, the equation is derived for spherical inclusions. Then the generalized result for ellipsoids is given.

The derivation of the MG equation [23] is based on combining the polarizability of an isolated particle with the averaged polarization effect of the effective medium. The drawback of MG is that when the volume filling ratio of spheres increases and the inclusion phase becomes connected, MG underestimates the effective permittivity. In the derivation of BS, the internal field of spheres is calculated by assuming that the sphere is surrounded by the effective permittivity $\varepsilon_{\mathrm{eff}}$, not by the permittivity of the environment phase ε_{e}. As a result, BS equation is in good agreement with the simulated and measured values of the effective permittivity when the volume fraction of inclusion is above the percolation threshold. However, when the volume fraction is below the percolation threshold, the BS tends to overestimate the effective permittivity.

The derivation of the new mixing equation follows the basic principles of the MG equation. The main difference from MG is that when the volume fraction of inclusions increases, the local electric field acting on each sphere approaches a similar field as in the BS mixing equation. The result is a differential equation for the unknown effective permittivity.

3.1. Mixture with spherical inclusions

Let us start with a single sphere with homogeneous permittivity ε_{i} in a homogeneous background with $\varepsilon_{\mathrm{eff}}$. The dipole moment of the sphere p can be expressed with the polarizability α

$$p = \alpha E_{\mathrm{L}}. \tag{3}$$

A local static electric field E_{L} acts on the sphere. The dipole moment of the sphere is defined as

$$p = (\varepsilon_{\mathrm{i}} - \varepsilon_{\mathrm{eff}})E_{\mathrm{i}}V, \tag{4}$$

where V is the volume of the sphere. The internal field E_i depends linearly on the local external electric field E_{L}

$$E_{\mathrm{i}} = \frac{3\varepsilon_{\mathrm{eff}}}{\varepsilon_{\mathrm{i}} + 2\varepsilon_{\mathrm{eff}}}E_{\mathrm{L}}. \tag{5}$$

By combining (4) and (5), the polarizability can be written as

$$\alpha = \frac{3\varepsilon_{\mathrm{eff}}(\varepsilon_{\mathrm{i}} - \varepsilon_{\mathrm{eff}})V}{\varepsilon_{\mathrm{i}} + 2\varepsilon_{\mathrm{eff}}}. \tag{6}$$

The electric far field of a dipole in a background with permittivity $\varepsilon_{\mathrm{eff}}$ is proportional to $p/\varepsilon_{\mathrm{eff}}$, which is equal to $(\varepsilon_{\mathrm{i}} - \varepsilon_{\mathrm{eff}})E_{\mathrm{i}}V/\varepsilon_{\mathrm{eff}}$. This is acting as the local field E_{L} to other dipoles, in addition to the primary field. If dipoles are added to the background so that the background permittivity changes by an amount $\Delta\varepsilon_{\mathrm{eff}}$, the local field acting on a dipole changes by the amount

$$\Delta E_{\mathrm{L}} = -\frac{\varepsilon_{\mathrm{i}}}{\varepsilon_{\mathrm{eff}}(\varepsilon_{\mathrm{i}} - \varepsilon_{\mathrm{eff}})}E_{\mathrm{L}}\Delta\varepsilon_{\mathrm{eff}}, \tag{7}$$

which comes from differentiating $p/\varepsilon_{\mathrm{eff}}$ with respect to $\varepsilon_{\mathrm{eff}}$. Here it is assumed that the electrical contrast $\varepsilon_{\mathrm{i}}/\varepsilon_{\mathrm{e}}$ between inclusions and the environment is relatively large, so the internal field of spheres is small. In that case we can use the first order approximation $\Delta E_{\mathrm{i}} = 0$.

When adding more dipoles to the mixture, only the local field of each sphere is changed, not the local permittivity around each sphere. The change in the dipole moment is also calculated by the change in the local field $\Delta p = \alpha\Delta E_{\mathrm{L}}$.

However, we need to link the change in the number of dipoles to the change in the effective permittivity. The corresponding change in the polarizability $\Delta\alpha$ which would result in the same change in the dipole moment is

$$\alpha\Delta E_{\mathrm{L}} = -\Delta\alpha E_{\mathrm{L}}. \tag{8}$$

From (6) to (8) the change in the polarizability is

$$\Delta\alpha = \frac{3V\varepsilon_{\mathrm{i}}}{\varepsilon_{\mathrm{i}} + 2\varepsilon_{\mathrm{eff}}}\Delta\varepsilon_{\mathrm{eff}}. \tag{9}$$

The effective permittivity of a mixture, where the original background permittivity is ε_e and a differential amount of spheres is added, can be calculated from the Taylor expansion:

$$\Delta\varepsilon_{\text{eff}}/\varepsilon_e = n\Delta\alpha/\varepsilon_e + \alpha\Delta n/\varepsilon_e, \tag{10}$$

where n is the number of spheres in the mixture and Δn is the change in the number of spheres. By substituting (6) and (9) to (10), we can write

$$\frac{\Delta\varepsilon_{\text{eff}}}{\varepsilon_e} = \frac{3\varepsilon_{\text{eff}}(\varepsilon_i - \varepsilon_{\text{eff}})}{\varepsilon_e(\varepsilon_i + 2\varepsilon_{\text{eff}})}\Delta f + \frac{3f\varepsilon_i}{\varepsilon_e(\varepsilon_i + 2\varepsilon_{\text{eff}})}\Delta\varepsilon_{\text{eff}}, \tag{11}$$

where $f = nV$ is the volume fraction of spheres. The corresponding differential equation finally gives us the resulting differential mixing rule

$$\frac{\mathrm{d}\varepsilon_{\text{eff}}}{\mathrm{d}f} = \frac{3\varepsilon_e(\varepsilon_i - \varepsilon_{\text{eff}})}{\varepsilon_i + 2\varepsilon_{\text{eff}} - 3f\varepsilon_i} \tag{12}$$

with the initial value $\varepsilon_{\text{eff}} = \varepsilon_e$ for zero filling value $f = 0$.

This differential equation is easy to solve numerically starting from $\varepsilon_{\text{eff}} = \varepsilon_e$ with $f = 0$. For practical reasons it is actually easier to solve the inverse function $\mathrm{d}f/\mathrm{d}\varepsilon_{\text{eff}}$ especially if the electrical contrast between ε_i and ε_e is large. Even if no limiting value for $f = 1$ is assumed, the limit for ε_{eff} seems to be in ε_i with all filling ratios. If the inverse $\mathrm{d}f/\mathrm{d}\varepsilon_{\text{eff}}$ is solved for $\varepsilon_e \leqslant \varepsilon_{\text{eff}} \leqslant \varepsilon_i$, then volume filling ratios are always exactly in the range $0 \leqslant f \leqslant 1$.

The solution for the inverse function of the differential equation with real values of ε_i and ε_e reads

$$f = 1 - \frac{1}{3}\frac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i - \varepsilon_e}\left(2 + \left(\frac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i - \varepsilon_e}\right)^{\varepsilon_i/\varepsilon_e - 1}\right). \tag{13}$$

For lossless materials $\varepsilon_e < \varepsilon_{\text{eff}} < \varepsilon_i$ and therefore the inverse function can be used by giving values for the effective permittivity ε_{eff} and by solving the corresponding volume fraction f.

3.2. Ellipsoidal inclusions

The differential equation for the effective permittivity of a mixture of randomly oriented ellipsoids can be derived in a similar way. The result reads

$$\frac{\mathrm{d}\varepsilon_{\text{eff}}}{\mathrm{d}f} = \varepsilon_e(\varepsilon_i - \varepsilon_{\text{eff}})\frac{\displaystyle\sum_{j=x,y,z}\left(\varepsilon_{\text{eff}} + N_j(\varepsilon_i - \varepsilon_{\text{eff}})\right)^{-1}}{3 - f\varepsilon_i\displaystyle\sum_{j=x,y,z}\left(\varepsilon_{\text{eff}} + N_j(\varepsilon_i - \varepsilon_{\text{eff}})\right)^{-1}}. \tag{14}$$

The effective permittivity of aligned ellipsoids is anisotropic. In general it has three components $\varepsilon_{\text{eff},x}$, $\varepsilon_{\text{eff},y}$ and $\varepsilon_{\text{eff},z}$:

$$\frac{\mathrm{d}\varepsilon_{\text{eff},j}}{\mathrm{d}f} = \frac{\varepsilon_e(\varepsilon_i - \varepsilon_{\text{eff},j})}{\varepsilon_{\text{eff},j} + N_j(\varepsilon_i - \varepsilon_{\text{eff},j}) - f\varepsilon_i}. \tag{15}$$

The solution of the inverse function for lossless ellipsoids reads

$$f = 1 + (N_j - 1)\frac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i - \varepsilon_e} - N_j\left(\frac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i - \varepsilon_e}\right)^{\varepsilon_i/\varepsilon_e}. \tag{16}$$

3.3. Percolation model

The solution for the effective permittivity can also be used to calculate the effective electrical or heat conductivities or the effective magnetic permeability of a mixture. For example, to calculate the effective electrical conductivity, permittivity ε is replaced with conductivity σ in equation (12)–(16). In some applications, such as when calculating the electrical conductivity of a polymer–metal composite consisting of metal powder in polymer matrix, the percolation threshold is an important parameter. The percolation threshold is the critical volume fraction of metal in the composite at which the metal phase becomes connected and the effective conductivity increases rapidly. Below the percolation threshold, the composite is an insulator and above the threshold it is a conductor.

Sometimes the percolation threshold of the composite is known or can be estimated instead of the shape of individual inclusions. In such a case a model with the percolation threshold ϕ as a parameter is useful. According to the new mixing model of this paper, the effective conductivity with ϕ as a parameter reads

$$\frac{\mathrm{d}\sigma_{\text{eff}}}{\mathrm{d}f} = \frac{\sigma_e(\sigma_i - \sigma_{\text{eff}})}{\sigma_{\text{eff}} + \phi(\sigma_i - \sigma_{\text{eff}}) - f\sigma_i}. \tag{17}$$

The solution for real σ_e and σ_i is

$$f = 1 + (\phi - 1)\frac{\sigma_i - \sigma_{\text{eff}}}{\sigma_i - \sigma_e} - \phi\left(\frac{\sigma_i - \sigma_{\text{eff}}}{\sigma_i - \sigma_e}\right)^{\sigma_i/\sigma_e}, \tag{18}$$

where σ_i is the conductivity of conductive inclusions, σ_e is the conductivity of the insulator phase and σ_{eff} is the effective conductivity of the composite.

4. Properties of the differential mixing equation

For the initial condition that in the case of vanishing volume fraction of inclusions the effective permittivity is equal to that of the environment, the full filling gives that the effective permittivity becomes equal to that of the inclusions, in other words

$$f = 0, \qquad \epsilon_{\text{eff}} = \epsilon_e \quad \Rightarrow \quad f = 1, \qquad \epsilon_{\text{eff}} = \epsilon_i. \tag{19}$$

For low volume fractions ($f \ll 1$), we can expand the solution for the effective permittivity as

$$\epsilon_{\text{eff}} = \epsilon_e(1 + a_1 f + a_2 f^2 + a_3 f^3 + \cdots), \tag{20}$$

substitute it into the differential equation (12), and solve for the coefficients a_i. The result for the three first terms is

$$a_1 = 3\frac{\epsilon_i - \epsilon_e}{\epsilon_i + 2\epsilon_e}, \tag{21}$$

$$a_2 = \frac{9}{2}\frac{\epsilon_i(\epsilon_i - \epsilon_e)^2}{(\epsilon_i + 2\epsilon_e)^3}, \tag{22}$$

$$a_3 = \frac{9}{2}\frac{\epsilon_i(\epsilon_i - \epsilon_e)^2(2\epsilon_i^2 - 3\epsilon_i\epsilon_e + 4\epsilon_e^2)}{(\epsilon_i + 2\epsilon_e)^5}. \tag{23}$$

It is interesting to compare this low-filling behaviour of the differential mixing equation to classical mixing rules, like

Maxwell Garnett and Bruggeman symmetric. These are contained in the unified mixing model [12]

$$\frac{\epsilon_{\mathrm{eff}}-\epsilon_{\mathrm{e}}}{\epsilon_{\mathrm{eff}}+2\epsilon_{\mathrm{e}}+\nu(\epsilon_{\mathrm{eff}}-\epsilon_{\mathrm{e}})}=f\frac{\epsilon_{\mathrm{i}}-\epsilon_{\mathrm{e}}}{\epsilon_{\mathrm{i}}+2\epsilon_{\mathrm{e}}+\nu(\epsilon_{\mathrm{eff}}-\epsilon_{\mathrm{e}})}. \tag{24}$$

This formula contains a dimensionless parameter ν. For different choices of ν, the previous mixing rules are recovered: $\nu=0$ gives the MG rule, $\nu=2$ gives the BS formula and $\nu=3$ gives the Coherent potential approximation.

The perturbation expansion for small values of f gives us

$$\begin{aligned}\epsilon_{\mathrm{eff}}=\varepsilon_{\mathrm{e}}&+3\varepsilon_{\mathrm{e}}\frac{\varepsilon_{\mathrm{i}}-\varepsilon_{\mathrm{e}}}{\varepsilon_{\mathrm{i}}+2\varepsilon_{\mathrm{e}}}f+3\varepsilon_{\mathrm{e}}\left(\frac{\varepsilon_{\mathrm{i}}-\varepsilon_{\mathrm{e}}}{\varepsilon_{\mathrm{i}}+2\varepsilon_{\mathrm{e}}}\right)^2\left(1+\nu\frac{\varepsilon_{\mathrm{i}}-\varepsilon_{\mathrm{e}}}{\varepsilon_{\mathrm{i}}+2\varepsilon_{\mathrm{e}}}\right)f^2\\&+3\varepsilon_{\mathrm{e}}\left(\frac{\varepsilon_{\mathrm{i}}-\varepsilon_{\mathrm{e}}}{\varepsilon_{\mathrm{i}}+2\varepsilon_{\mathrm{e}}}\right)^2\left(1+\nu\frac{\varepsilon_{\mathrm{i}}-\varepsilon_{\mathrm{e}}}{\varepsilon_{\mathrm{i}}+2\varepsilon_{\mathrm{e}}}\right)\\&\times\left(1+\nu\frac{\varepsilon_{\mathrm{i}}-4\varepsilon_{\mathrm{e}}}{\varepsilon_{\mathrm{i}}+2\varepsilon_{\mathrm{e}}}\right)f^3+\cdots.\end{aligned} \tag{25}$$

The linear term in f is seen to be independent of ν. It is indeed well known that the slope with which the effective permittivity starts to grow is the same for many mixing rules. And the slope is also the same for the differential mixing formula (the coefficient a_1).

Which value of ν would give a mixing rule that would be closest with the new equation? Let us balance the second power of f in the expansions (the a_2 coefficient). This gives us

$$\nu=\frac{1}{2}\cdot\frac{\epsilon_{\mathrm{i}}-4\epsilon_{\mathrm{e}}}{\epsilon_{\mathrm{i}}-\epsilon_{\mathrm{e}}}. \tag{26}$$

This means that for large permittivity contrasts ($\epsilon_{\mathrm{i}}/\epsilon_{\mathrm{e}}\gg 1$), the differential equation for small volume fractions gives the same predictions as the unified formula with $\nu=1/2$, which is close to Maxwell Garnett mixing. It becomes even closer to Maxwell Garnett when the contrast decreases. However, when the contrast goes below 4, the equivalent ν becomes negative and this is no longer the domain of the differential mixing equation.

The other limit is the high-volume filling; in other words f is close to unity. To find the slope there, let us plug the linear expansion $\epsilon_{\mathrm{eff}}\approx\epsilon_{\mathrm{i}}-k(1-f)$ into the differential equation (12), which gives us the slope k as $k=3/2(\varepsilon_{\mathrm{i}}-\varepsilon_{\mathrm{e}})$. If this slope is set equal to the slope of the unified mixing formula (24) at $f=1$, we get the following value for the ν value that is 'closest' to the differential mixing equation for high-volume fractions:

$$\nu=\frac{2\varepsilon_{\mathrm{i}}-5\varepsilon_{\mathrm{e}}}{\varepsilon_{\mathrm{i}}-\varepsilon_{\mathrm{e}}}. \tag{27}$$

For high contrasts (the regime of the differential equation), this approaches $\nu=2$, which is the Bruggeman mixing rule.

5. Comparisons and discussion

Let us analyse the predictions of the differential mixing formula.

5.1. Classical models

With respect to classical mixing relations for spherical inclusions we can make the following observations. In the low volume fraction limit $f\to 0$, the slope of the effective permittivity is defined by the polarizability of an isolated sphere. This is correct in Maxwell Garnett (MG), Bruggeman symmetric (BS) and coherent potential (CP) formulae and the proposed differential mixing equation has this same derivative with low-filling ratios. It has also been shown [9,24] that with slightly larger volume filling ratios only Maxwell Garnett terms are correct for ordered cubic centred lattices. However, in natural mixtures the inclusions are often randomly distributed and the higher order derivatives also deviate accordingly.

All mixing rules in table 1 predict fairly similar results when the contrast between the inclusion and the environment phase is small. In figure 2 the new mixing equation is shown as a function of volume fraction of spherical inclusions with permittivities $\varepsilon_{\mathrm{i}}=10$ and $\varepsilon_{\mathrm{e}}=1$ in a linear scale. On the left-hand side the differential equation is presented with Maxwell Garnett (MG), Bruggeman (BS) and coherent potential (CP) formulae and on the right-hand side with Looyenga (LO), Bruggeman non-symmetric (BN) and with Sen–Scala–Cohen (SSC) formulae. In figure 3 the same formulae are plotted with a higher contrast, permittivities $\varepsilon_{\mathrm{i}}=100$ and $\varepsilon_{\mathrm{e}}=1$. Note that the vertical axis is logarithmic.

Figures 2 and 3 show that the effective permittivity according to the differential mixing equation shifts smoothly from Maxwell Garnett to the symmetric Bruggeman as the volume fraction of spheres increases. Figure 3 shows clearly that the derivative in the limit $f\to 0$ is the same for all models on the left-hand side, but on the right-hand side it is very different for Looyenga and Sen–Scala–Cohen models.

In figure 4, the logarithm of effective permittivity of randomly oriented and distributed ellipsoids and spheres is presented. Three solid lines correspond to the effective permittivity of a mixture of spheres and dashed lines the effective permittivity of ellipsoids with semi-axes $a_z=4$ and $a_y=a_z=1$. The upper curve in both sets corresponds to BS and the lower curve to the MG mixing equations. The middle curve is the new differential mixing equation. The permittivity of inclusions is 1000 and the permittivity of the background is 4. These values could be typical for a mixtures of high permittivity ceramic inclusions in a polymer matrix.

It can be seen that all models predict the effective permittivity to be larger for ellipsoidal inclusions compared with spherical inclusions. The MG and BS mixing equations differ significantly starting with very small volume fractions of inclusions, especially for ellipsoidal inclusions. For composites where inclusions are well dispersed, the measured values should follow the MG with small volume fractions of inclusions and BS with high-volume fractions of inclusions. However, the gap between these models is so large that these models could be applied at the same time. In this respect, the new mixing equation provides a very useful practical tool in the design of composites. It combines a strong predictive power over the whole range of volume fractions and it also allows the inclusion shape to be modelled as ellipsoids.

When the shape of the inclusions is changed from the sphere, the percolation threshold decreases as it becomes more likely for the inclusions to touch. As a result, the model can be used simultaneously to predict accurate values with small volume fractions of inclusions and also to predict the increase in the effective permittivity at the onset of the

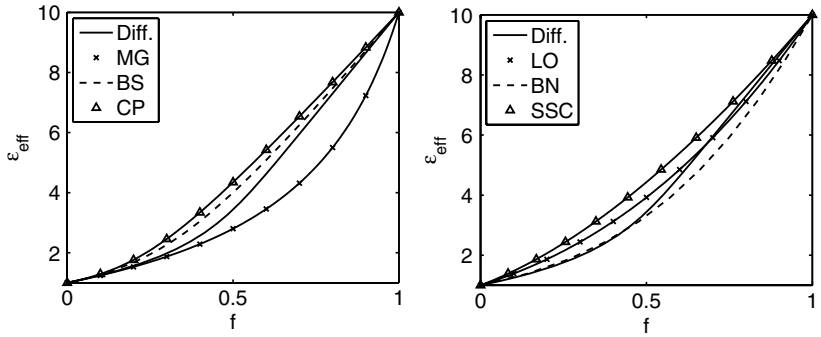


Figure 2. Effective permittivity as a function of the volume filling ratio of spheres. The relative permittivity of inclusions is $\varepsilon_i = 10$ and that of the environment is $\varepsilon_e = 1$. The label 'Diff.' refers to the proposed differential mixing equation (12), and MG, BS, CP, LO, BN and SSC refer to the various mixing rules given in table 1.

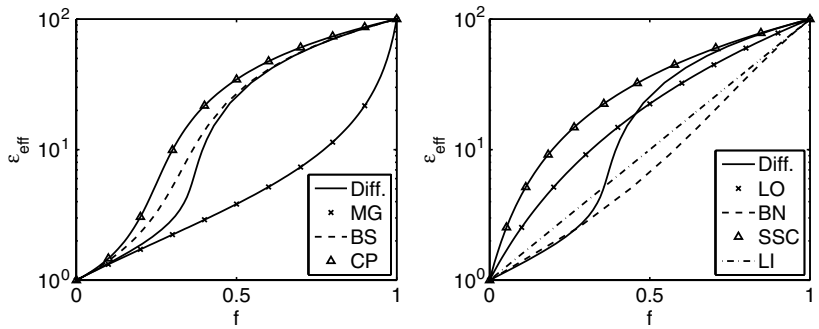


Figure 3. As in figure 2, but now the relative permittivities are $\varepsilon_i = 100$ and $\varepsilon_e = 1$ and the vertical scale is logarithmic.

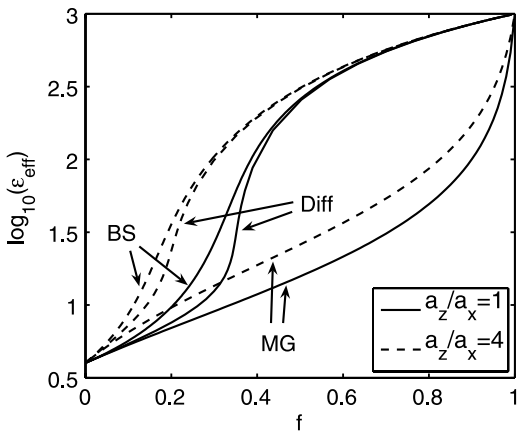


Figure 4. The logarithm of the effective permittivity of a mixture of randomly oriented prolate ellipsoids (dashed lines) with semi-axes $a_z = 4$, $a_x = a_y = 1$, and spheres (solid lines). The upper line in both sets corresponds to BS, the middle line to the differential equation of the present paper for ellipsoidal inclusions (14) and the lower line corresponds to MG. Permittivities are $\varepsilon_i = 1000$ for the inclusions and $\varepsilon_e = 4$ for the environment.

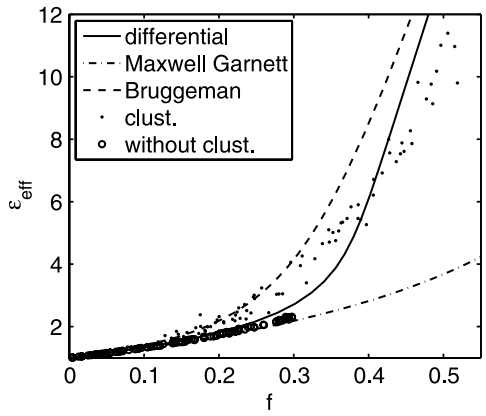


Figure 5. Effective permittivity as a function of the volume filling ratio of spheres. The permittivity of spheres is $\varepsilon_i = 51$ and the permittivity of the background is $\varepsilon_e = 1$. Lines represent different analytical models and dots and circles numerically calculated random samples from [25].

percolation. Therefore it can be used to compare how the effective permittivity would change as the shape of inclusions is changed.

5.2. Comparison with numerical results

In figure 5 the differential mixing equation is compared against numerical finite difference simulations from [25] with permittivities $\varepsilon_i = 51$ and $\varepsilon_e = 1$. Dots and circles represent simulated effective permittivities for Monte Carlo samples of mixtures of spheres. Dots are simulations with spheres which are allowed to overlap and form clusters, and open circles are simulated with spheres without clustering; in other words in that case the spheres do not touch.

In the case where spheres can form clusters, the effective permittivity is greater than in the case where clusters are not allowed because the normalized polarizability of clusters is greater than that of individual spheres. In the non-clustering case, percolation was not possible and therefore the highest volume fraction that can be simulated is near the percolation

threshold. The differential equation lies between the clustering and non-clustering case. Note that the case where clusters are allowed has a different morphology than what was assumed for the differential equation: in the algorithm, spheres are allowed to overlap and to form new more complex shapes.

5.3. Percolation and comparison with experimental values

Another interesting phenomenon in mixture behaviour is percolation which happens clearly for high parameter contrasts between the mixing phases. Figure 4 shows that both Bruggeman and the new mixing equation produce a percolation threshold close to $f \approx 0.3$, for spherical inclusions. The difference is that the percolation is stronger for the new equation. On the other hand, MG does not show a clear percolation. Another way of expressing this is that the percolation threshold for MG is $f = 1$, which means the effective permittivity starts to increase rapidly when the mixture is completely filled with inclusions. In practice we would suspect the percolation to take place when the spheres touch each other. The random arrangement of spheres has been shown to have a percolation threshold close to $f = 0.3$ [26]. The percolation threshold of CP formula for spheres is known to be 0.25 [12].

If the new differential equation is used to model the effective conductivity of a random mixture of conductive inclusions in a non-conductive matrix, the percolation is much stronger. In figure 6 the differential model (18) for the effective conductivity as a function of volume of metal in the composite is presented for a metal–polymer composite. Triangles are measured values taken from [27] for a composite, which is made with randomly distributed copper particles and polyethylene. The values for σ_i and σ_e (see the figure caption) are taken from [27] and the parameter for the percolation threshold $\phi = 0.06$ was found suitable. The differential formula seems to model the effective conductivity reasonably well with all volume fractions of metallic powder. In [27], the model adjusted to the measured values had six adjustable parameters, which is much more than three parameters needed for (17). More importantly, all parameters used in equation (17) have a clear physical meaning: conductivity of the polymer, conductivity of the metal and the percolation threshold of the material. Note that the new model predicts very flat effective conductivity below the percolation threshold, which is very typical behaviour for metal-filled polymers. This example illustrates how the differential equation can be used to model accurately the effective conductivity of the composite with low volume filling ratios and still take the percolation into account. The model is valid if metallic inclusions are well mixed.

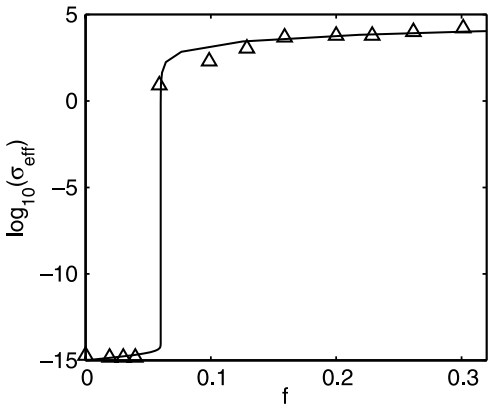


Figure 6. Measured values taken from [27] for the conductivity of a mixture of pressed copper and plastic powders, compared against equation (17) with $\sigma_e = 1 \times 10^{-15}$ and $\sigma_i = 4 \cdot 10^4$ and $\phi = 0.06$ (marked with the solid line). Note the logarithmic scale of the effective conductivity.

6. Conclusions

A new differential mixing equation for the effective permittivity of a random mixture of spheres and ellipsoids is presented and it is compared with numerical simulations and measurements from the literature. The proposed equation is close to the Maxwell Garnett mixing rule with low volume ratios of spheres and it approaches the Bruggeman mixing equation when the volume fraction increases. This behaviour is independent of electrical contrast between inclusions and the environment. It combines the small volume filling ratio properties of the Maxwell Garnett equation to the percolation properties of the Bruggeman symmetric equation. The percolation predicted by the differential equation occurs with the same volume fraction of inclusions as with the Bruggeman formula, but the percolation is stronger.

The differential mixing equation is derived especially for high electrical contrast between inclusions and the background. Therefore it can also be applied when calculating the effective static conductivity of a mixture of non-ideal metallic inclusions in the insulating background. For this purpose, a model which has the percolation threshold as a parameter instead of the depolarization factors was presented.

The model is good for applications where inclusions are uniformly and randomly distributed to the background. Therefore it offers a good starting point for the material engineering: the effective permittivity/conductivity/permeability can be modelled with all volume fractions of inclusions and with different inclusion shapes (or percolation thresholds) without any adjustable parameters. The main advantage of the new method is that the low volume-filling-ratio properties can be modelled accurately while the onset of the percolation is taken into account at the same time. This helps to compare the properties of different material combinations with varying material parameters and inclusion shapes. Deviations from uniform particle distribution in a composite (for example non-uniform clusterization of particles) depends on the manufacturing process and its effect on the effective material parameters is therefore very difficult to predict. However, a model which is known to work well under certain well-defined conditions is a very useful starting point for any material engineering application.

Acknowledgments

We gratefully acknowledge Professor Jukka Sarvas for solving the inverse of the differential equation and Dr Kimmo Kärkkäinen for giving us his numerical simulations from [25]. L Jylhä would like to thank the Graduate School in Electronics, Telecommunications and Automation, for financial support. The work has been supported by the Academy of Finland.

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